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GENERAL CONSIDERATIONS CONCERNING METASTABLE SPECIES

Guy Watel

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~~THE METASTABLE SPECIES~~

GENERAL CONSIDERATIONS CONCERNING METASTABLE SPECIES

Guy Watel

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ABSTRACT. The metastable species are atoms, molecules, or ions in excited states whose lifetimes are sufficiently long for their return to ground states, under laboratory conditions, by the action of an outside phenomenon (electric or magnetic field, collision with other particles or the walls). This literature survey concerns the metastable atoms which have been most studied up to now: He, Ne, H, Hg, Ar, and Kr.

Cover Page Source

CHAPTER I. FORMATION-PRODUCTION

The metastable species are formed in gas discharges. The medium is complex and there are collisions with the walls, atoms, electrons, ions, and other metastable species. The properties of metastable species in pulse discharges have been involved in a large number of studies (Chapter III). /3*

The metastable species are formed during bombardment of a metal surface by ions. Oliphant (1929), Greene (1950) and Hagstrum (1961) have studied the formation of metastable species by impact with ions of He^+, Ne^+, Ar^+, H^+ on a variety of surfaces (W, Mo, Si, Ge).

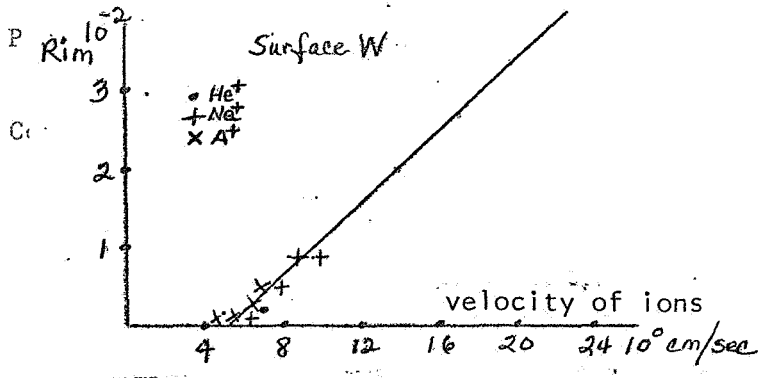
A certain number of ions are reflected in the form of ions, the ratio Rii varying from 0.0004 to 0.002, according to the nature of the metal and independently of the energy (in the range from 10 to 1000 eV). Others are reemitted in the form of excited neutrons, the ratio Rim varying from the value Rii (for 10 eV) to 0.04 (for 1000 eV). The maximum value measured is about 0.2 (at 1000 eV) for the transformation $He^+ \rightarrow He^m$ at surface (1,1,1) of a germanium crystal.

Experimenters who wish to study the properties of metastable species have tried to obtain high densities or flux and less complex media. It is therefore absolutely necessary to use very pure gases (impurities $< 10^{-4}$), and very good residual vacua ($< 10^{-10}$ mm Hg), and to bake the enclosures whose walls are sometimes gold plated.

*Numbers in the margin indicate pagination in the foreign text.

$I_{mi\,rastables} = (Rim)(I_{ions})$

H_R^+ eq	Rim W	Rim Ge(111)
100	0.0019	0.0015
200	0.0088	0.023
400	0.020	0.077
600	0.024	0.12
800	0.034	0.15
1000	0.039	0.20



PRODUCTION OF METASTABLES

Should be reflected in TC

/4

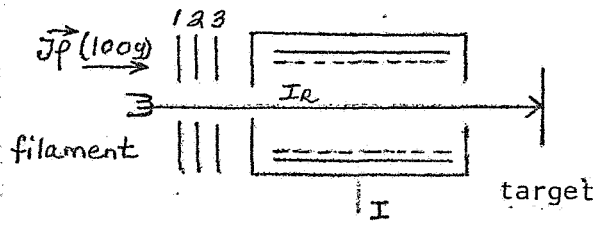
1) Electron Bombardment of a Gas:

Atoms of gas are excited by electrons. The production of metastable species is characterized by the value of the effective cross section σ_E defined by the relationship $I_M \approx \frac{I_e}{e} \sigma_\varepsilon n \ell$, I_M being the flux of metastable species formed by the electron beam of intensity Ie, energy E, and which travels over a length ℓ in a medium of density n. In the presence of a magnetic field we must take the actual length.

The densities obtained by this method are of the order of 10^{10} metastable particles per cm^3. Few ions are formed and by preventing the emission of electrons, there remain only metastable particles and neutrons within the enclosure.

Experimental devices - measurement of σ_E

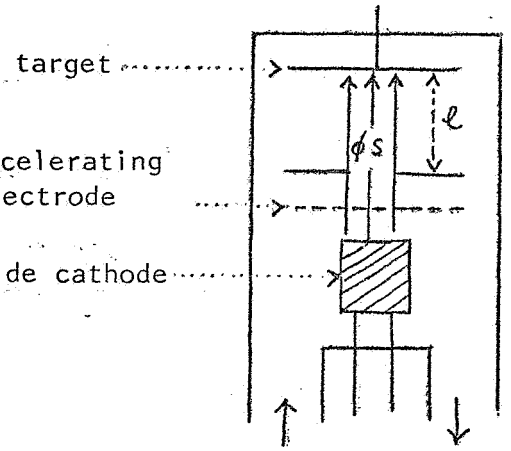
HELIUM DORRESTEIN (1942) SCHULZ (1957-59) HIGGINSON (1961-64)



A beam of electrons, which is made monokinetic by electrodes 1, 2, and 3, is focused by a magnetic field and traverses a chamber containing helium. The metastable particles formed are destroyed when they strike a metal wall where they are measured by secondary electron emission or by some other method (Chapter II-2, 3). The effective cross section is obtained by the relationship $\sigma_E = \frac{I \cdot G}{\gamma I_o n \ell}$ (γ is the coefficient of secondary electron emission; G is the correction factor due to the geometry of the device). Holt (1965) /5 uses an enclosure containing helium ($2 \cdot 10^{-4}$ mm Hg) and an electron gun and measures metastable species which are diffused by secondary electron emission. The metastable species 2^3S are separated from species 2^1S through the action

of an inhomogeneous magnetic field (Chapter II-1). Holt distinguishes the 2^1S from the excited states 2^3P through the action of an electric field (Chapter II-1). He measured the effective production cross section σ_E of the metastable species 2^1S only relatively.

NEON HADEISHI (1962-1965)



The mercury ions formed neutralize the electron beam

The electron gun is in the enclosure which is devoid of a magnetic field. The density of the metastable M, is measured by absorption of a beam of light (Chapter II-4). The number of metastable particles produced per cm^3 per second is $\frac{I_n}{s\ell} = \frac{J}{e}\sigma_\varepsilon n$, n being the density of the electron beam current of cross section S. The number of metastable particles which disappear per cm^3 per second is equal to $\frac{M}{\delta}$, δ being the lifetime of the metastable, and which is obtained from the absorption curve. For the steady state $\frac{J}{e}\sigma_\varepsilon n = \frac{M}{\delta}$

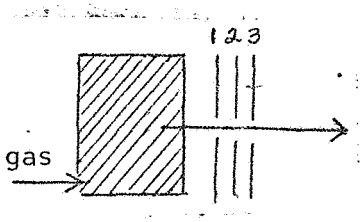
$\sigma_\varepsilon = \frac{M}{\delta} \Big/ \frac{J}{e} n$

MERCURY WEBB (1924) COULIETTE (1928): used this method to produce metastables $3P_0$.

HADEISHI (1965) produced metastables $3P_2$ by this method.

2) Production of a Beam of Metastable Particles: } should be reflected in T^2 /6

a) Beam Obtained by Diffusion



The metastable particles formed either by discharge or by electron bombardment diffuse through a hole pierced in the wall. Electrodes 1, 2, and 3 eliminate the ions and collimate the beam. This method produces a beam of metastable species having thermal energy, but with the drawback of super imposing upon it a beam of photons and neutrons.

Experimental devices and results:

HYDROGEN: the metastable species are formed in a Wood's discharge, a method proposed by Lamb (1950), but not used.

Page One Title

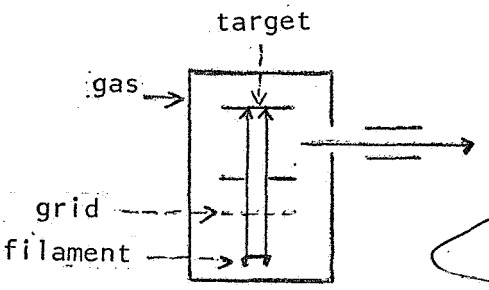
HELIUM STEBBING (1957) HASTED (1959): used a hot cathode discharge (100 volts, 180 mA). The resulting beam has a diameter of 0.2 mm and a density of $2 \cdot 10^{10}$ p/cm^3. Fite (1963) uses a high frequency discharge. Muschlitz (1960-62-63-64-65) and Holt (1965) use a gas bombarded with electrons.

Cover Page Title

NEON

Hasted (1959) uses a hot cathode discharge.

Fite (1963) uses a high frequency discharge.



b) Beam Obtained by Bombarding a Neutron Beam With Electrons /7

A beam of electrons with a velocity v_e meets a beam of atoms with a velocity at right angles. As in the case of the bombardment of a gas, the production of metastable species is characterized by the effective cross section σ_E defined by the relationship $I_M \propto \frac{I_e}{e} \cdot \sigma_E \cdot I_a \cdot \frac{(v_e^2 + v_a^2)^{\frac{1}{2}}}{v_e v_a} \cdot F$(Kieffer). E is the relative energy and F is a factor characterizing the intersection of the beams ($F = \frac{\int J_a(z) J_a(z)\, dz}{\int J_a(z)\, dz \int J_a(z)\, dz}$ $J_e(z)$, $J_a(z)$ being the space distribution functions of electron and ion beams in the z direction).

If the beams are homogeneous and if $v_a \ll v_e$

$$I_M \approx \frac{I_e}{e} \sigma_E I_a \frac{1}{v_a} \cdot \frac{1}{h} \qquad h = \int dz .$$

Experimenters prefer to measure the excitation function, that is, the number of metastable particles formed as a function of the energy of the electrons, the other parameters remaining constant. By normalizing this function, directly or indirectly, with a theoretical value, they obtained the effective cross section.

In order to measure this function account must be taken of the following:

1) the variation of space charge as a function of electron energy, which can modify the value of Ie. Lamb assumes the law for laminar electron beams

$(E = eV_s)$ $I_e = C \sqrt{\pi} V^{\frac{1}{2}}$

2) production of high level excited states by high energy electrons that may produce metastable particles which will return in cascades (Stebbing),

3) variation in direction of the atoms under impact of electrons. The electrons have sufficient energy to cause a change in direction of the atom at which the thermal energy is aimed. Calculation of the angles of deviation was made by Lamb and Stebbing (Figure 1-6), since the beam of atoms was not monokinetic, this deviation caused a spread of metastable products.

Experimental devices and results. /8

HYDROGEN LAMB (1950), HEBERIE (1956), LICHTEN (1959)

The atom beam is obtained by means of a furnace. The electron beam is laminar (Haeff). Measurement of the metastable products is made by secondary electron emission and action of an electric field (Chapter II-1). Lamb has measured the excitation function in arbitrary units. Lichten normalizes by means of Born's approximation for electrons of 40 electron volts. He gives an absolute value for 11.7 electron volts (Figure 1-7).

Stebbing (1960). The atom beam is emitted from a furnace, while the electron gun is conventional. It measures the ratio of effective cross sections of production of metastable σ_{2S} to those of excited states σ_{2P}. The atom beam is time modulated in order to eliminate the reactions of electrons with the residual vacuum. The excited states 2P are measured by emission of Lyman α photons while the 2S metastable particles are measured by the action of an electric field (Chapter II-1). The effective cross section σ_{2P} is obtained by normalizing to Born's approximation for electron of 400 eV. Using the value of the ratio σ_{2S}/σ_{2P}, Stebbing obtained the value $\sigma_{2S}(E)$ (Figure 1-8).

Lichten (1961), critiques the method used by Stebbing to measure the number of metastable products (Chapter II-4) and supplies a correction factor that reconciles Stebbing's results with his.

Hummer (1961), critiques the normalization used by Lichten (1959) and normalizes Lichten results with those of Stebbing's corrected by Lichten (Figures 1-9).

MERCURY

Lichten (1960), using an apparatus identical to that used in 1959 for hydrogen, measures the excitation function for the production of 3P2 in arbitrary units. The metastable particles are detected by secondary electron emission (Figures 1-10).

c) Beam Obtained by "Charge Exchange" Reaction /9

$$O^+ + X \rightarrow O^m + X^+$$

A beam of ions passes through a gas. There is an exchange of charge and the neutron formed may be in an excited state. The effective section for a process of charge exchange (all excitation) has been studied theoretically by Bates (1953), Hasted (1960-64), Massey (1949-52), and Cheshire (1965). The effective cross section is large when the difference ΔE of the internal energy of the two members of the reaction is small and when the ionization potential of the target particle is low. For a given value of ΔE, the effective cross section increases rapidly with relative speed v of the incident particle until $v = a\Delta E/h$ [a is the domain of action of the atoms (for helium, $a = 2 \cdot 10^{-8}$ cm)] and decreases slowly. In the case of resonance, $\Delta E = 0$, the effective cross section decreases slowly when v increases.

Experiment investigations and results.

HYDROGEN

Nadansky (1959) uses this method to produce a beam of polarized protons from metastable H2S.

Cristofori (1962-63) measures the excitation function for the production of metastable H2S by passage of a proton beam (7 to 40 KeV) through hydrogen and helium. He normalizes to the approximation by Born for an energy of 40 KeV (Figures 1-11).

Donnally (1964) measures the effective cross section of production of metastables H2S by passing a proton beam (0.2 to 3 KeV) through a thermically energized cesium atom beam. The cesium is chosen for its low ionization potential, 3.89 electron volts, which results in a reaction $H_1^+ + Cs \rightarrow H2S + Cs^+$ ($\Delta E = 0.49$) that is close to resonance (Figures 1-12).

Jaecks (1965) measures the excitation function for producing H2S metastable particles by passing a beam of protons and molecular hydrogen ions through different gases (Ar, Xe, He, Ne). /10

Process (1) is the most probable for helium no matter what the energy of hydrogen ions may be. Process (2) is the most probable for Ne, Ar, Xe with with high energy ions.

$$H_2^+ + X \rightarrow H_{2S} + H + X^+ \quad (-1)$$

$$H_2^+ + X \rightarrow H_{2S} + H^+ + X \quad (2)$$

Jaecks measures the number of excited (2P) atoms formed at the same time as the 2S metastable particles by means of their spontaneous emission of Lyman protons, then he measures the total number of states 2P and 2S by destroying the 2S types by means of an electric field (Chapter II-1). Knowing the effective cross section of production of the 2P excited state (Pretzer), then deduces σ_{2S}.

HELIUM

Barnett (1958), while studying the exchanges of charges in a He^+ ion beam (20 to 250 KeV) passing through various gases, noticed the formation of metastable He^m for helium and neon at low pressure (mean free path approximately the dimensions of the enclosures). He made no measurements.

Lorentz (1965) measures the effective cross sections of charge exchange for He^+ ions (15 to 1500 ev) passing through vapors of Cs and Rb. These effective cross sections are large (10^{-14} cm^2). Lorentz assumes that the helium atom formed is in an excited or metastable state which makes the reaction almost a resonant one.

ARGON

Lorentz (1965) measures the effective cross sections for charge exchange for Ar^+ ions traversing Cs and Rb vapors. As in the case of helium, the argon atom formed is assumed to be in an excited or metastable state.

HELIUM

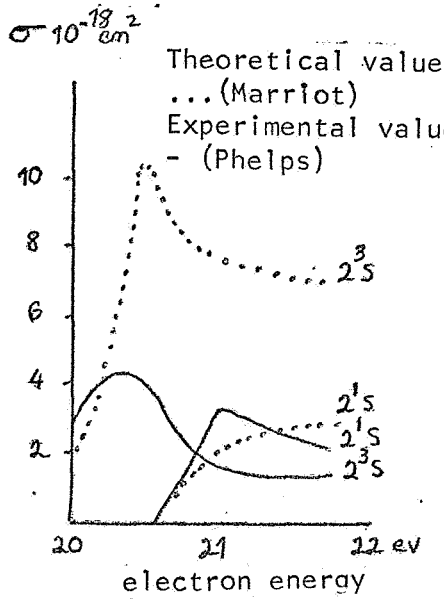


Figure I-1

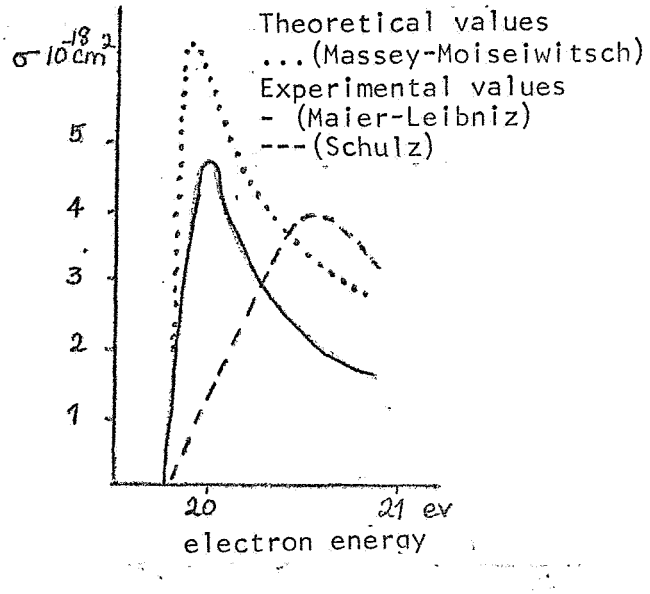
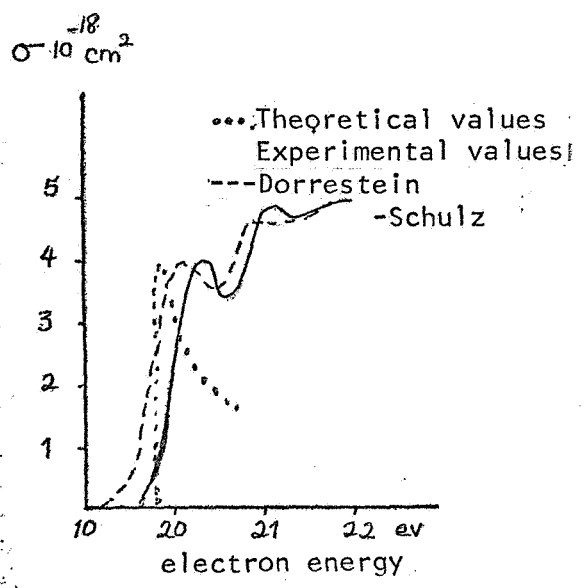


Figure I-2(HASTED)



Experimental values

- 2^1S $\sigma_{max} = 1,5 \pm 0,5\ 10^{-18}\ cm^2$ (21.22ev) (HOLT)

normalized to σ_{max} 2^3S of SCHULZ)

- 2^3S $\sigma_{max} = 2,6 \pm 0,4\ 10^{-18}\ cm^2$ (20.4 ev) (HIGGINSON)

Figure I-3

NEON

	19 ev	23 ev
σ	$0,48 \cdot 10^{-19}\ cm^2$ (1,23 mm Hg) $1,95 \cdot 10^{-19}\ cm^2$ (1,63 mm Hg)	
σ		$1,54 \cdot 10^{-19}\ cm^2$ (0,41 mm Hg) $0,63 \cdot 10^{-19}\ cm^2$ (0,69 mm Hg)

Figure I-4 (HADEISHI)

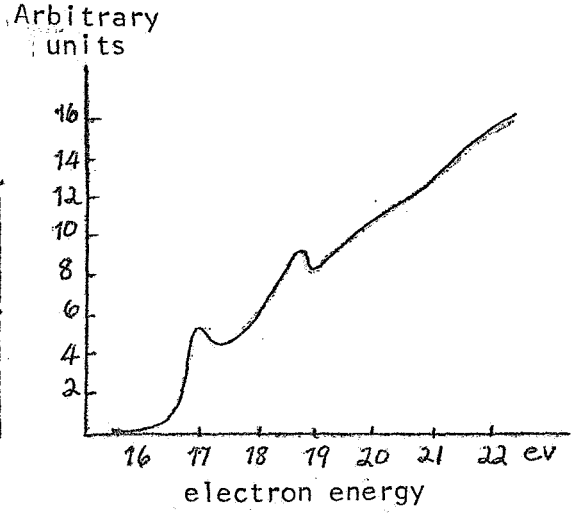


Figure I-5 (DORRESTEIN)

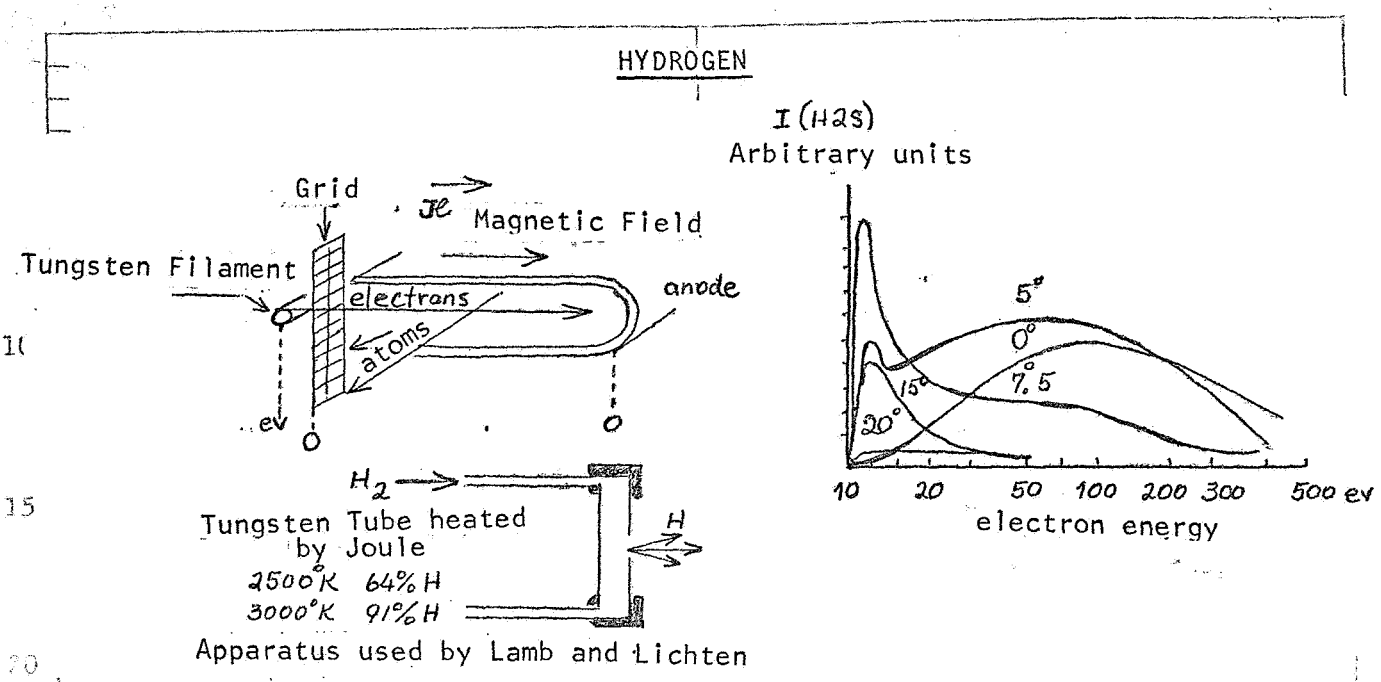


Figure I-6 (STEBBING)

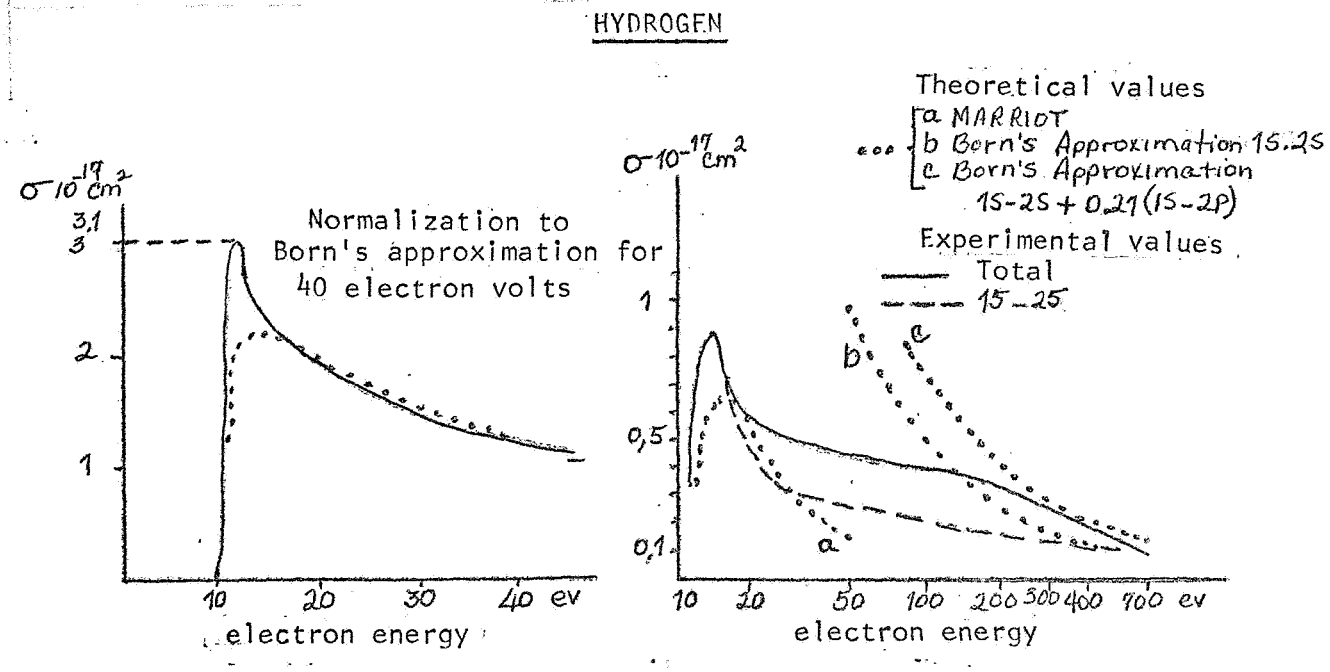


Figure I-7 (LICHTEN)

Figure I-8 (STEBBING)

MERCURY

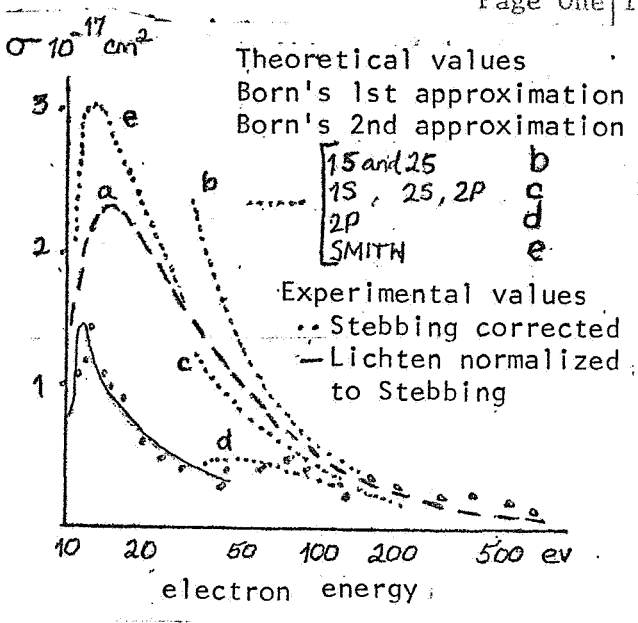


Figure I-9 (HUMMER)

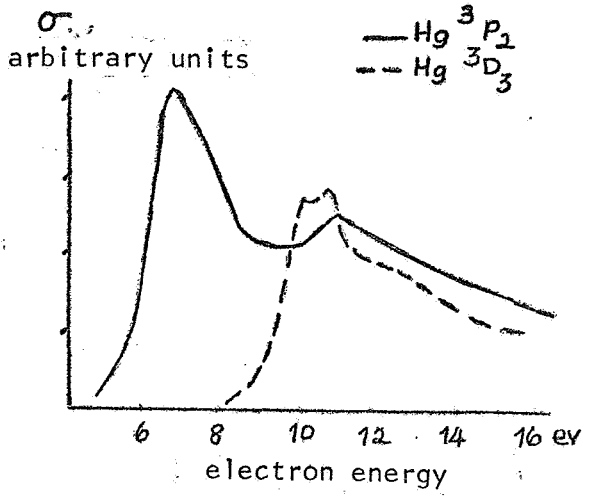


Figure I-10 (LICHTEN-DERMOTT)

HYDROGEN

$H_1^+ + H_2$, OR He

normalization to Born's approximation for 40 Kev.

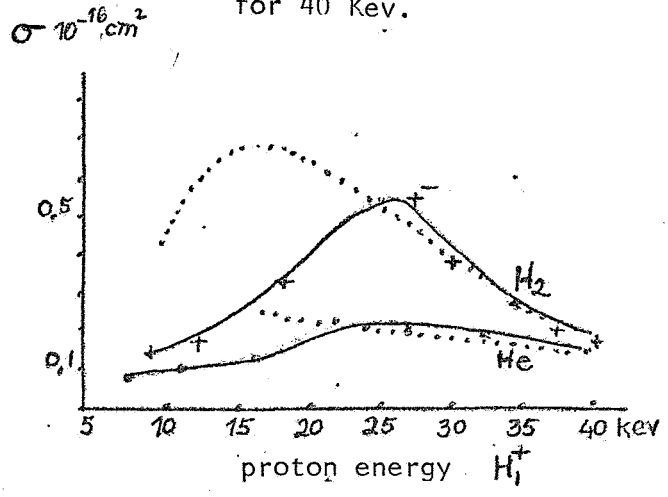


Figure I-11 (CRISTOFORI)

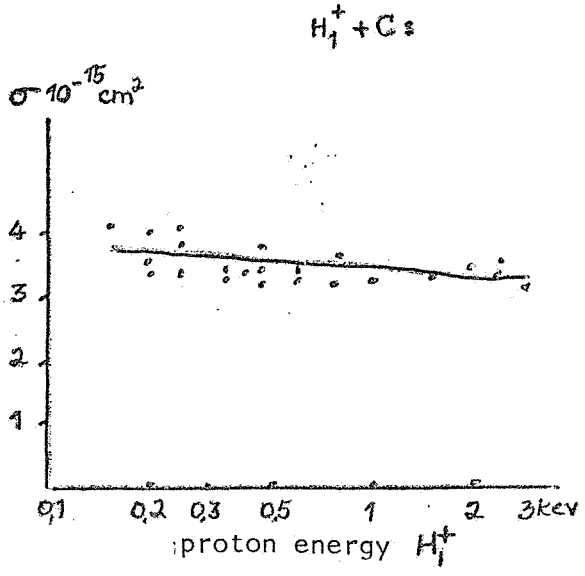


Figure I-12 (DONNALLY)

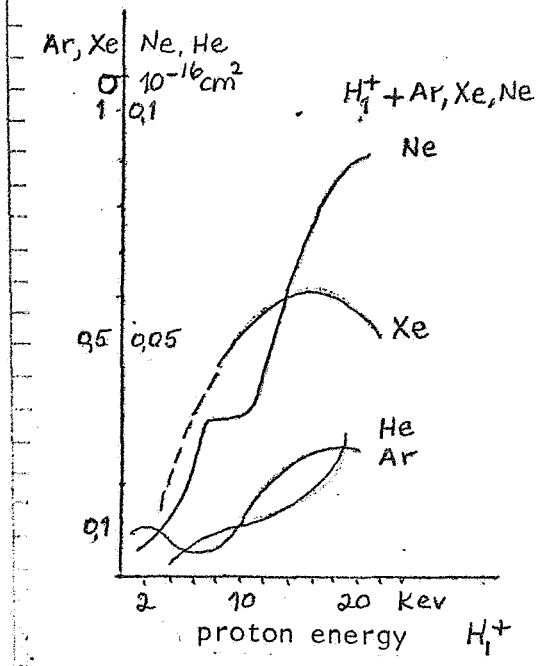


Figure I-13 (JAECKS)

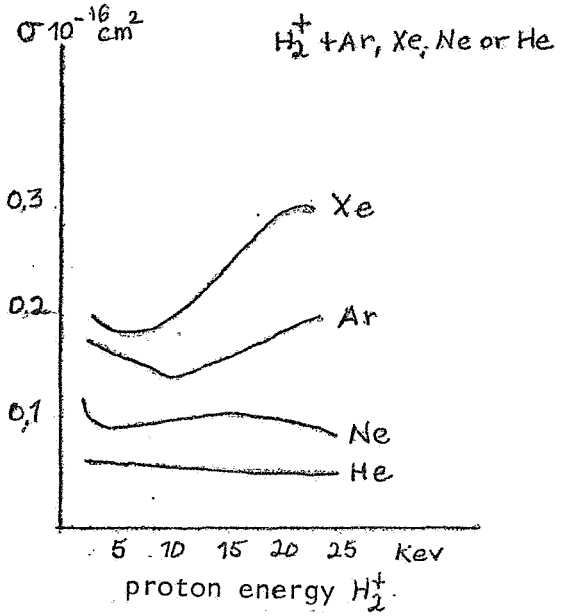


Figure I-14 (JAECKS)

CHAPTER II- DETECTION /11

Certain properties of metastable species are used to detect them and measure their density or flux.

1) Action of an Electric or Magnetic Field

HYDROGEN

The lifetime of type H2S metastable species which are placed in an electric or magnetic field depends on the value of this field. The metastable species passes into the 2P excited state which returns to the fundamental state by emitting a Lyman α photon that is detected by a counter.

This phenomenon has been studied theoretically by Luder (Figure II-1, II-2) and Bethe. It has been studied experimentally by Sellin and Jaeck for the values of field from 100 to 1000 volts/cm. Zernik studies the action of a high frequency electric field.

Experimental apparatus:

This method is used to measure the flux of metastable species H2S. The beam passes through an electric field while a light particle counter (Fite, 1958) measures the amount of light emitted over a certain solid angle. All of the metastable species are destroyed when the signal measured is independent

of the value of field. It is necessary:

1) to use a filter allowing the Lyman α ray to pass. (In general, it is made of dry oxygen gas passed between two windows of LIF).

2) To eliminate or measure the emission of Lyman α rays which are not produced by the destruction of metastable species (presence of excited states, electron collision with residual gas or walls, etc.).

3) To know the space distribution function of the emitted radiation in order to obtain the emission throughout all space based on the measurement made for a certain solid angle. /12

Lichten (1959) assumes an isotropic distribution. Stebbing (1960) considers that the distribution is not isotropic. Using the measurement made in a direction perpendicular to the electric field $\sigma_{90°}$, he deduces σ_{2S} by means of the relationship $\sigma_{2S} = 2/3\ \sigma_{90°}$. Lichten (1962) does not assume Stebbing's hypothesis and reestablishes the 3/2 factor to compare his results to those of Stebbing. Jaecks (1965) assumes an isotropic distribution. Cristofori and Donnally have also used this method.

In spite of the precautions taken, that is, nonreflecting gold plated walls, baking, and focusing of electrons by means of a magnetic field, there is a signal present even in the absence of an electric field which constitutes a systematic error for the absolute measurements.

Jaecks (1965) evaluates these errors by replacing the proton beam by a beam of helium ions and finds that the observed signal produces a systematic error.

HELIUM

Holtz utilizes a strong electric field (340,000 V/cm) to take the 2'S metastable species to the excited state 2'P.

Action of a nonhomogeneous magnetic field:

An atom with a magnetic moment $\vec{\mu}$ which is placed in a magnetic field $\vec{H}$, undergoes a variation in energy $\Delta w = \mu H$, H being the component of $\vec{\mu}$ in the direction H. It is acted on by a force $F_x = N_z \frac{\partial H}{\partial x}$, $F_y \ldots F_y \ldots$. If the field H is homogeneous, $\frac{\partial H}{\partial x} = \frac{\partial K}{\partial y} = \frac{\partial H}{\partial z} = 0$, the force is zero. If the field is not homogeneous, it has the following components: F_x, F_y, F_z.

For an excited atom [illegible]

$\mu_0 = 0{,}918\ 10^{-20}$ erg gauss^{-1} (Born's magnetron)

Mg is given by Fraser /13

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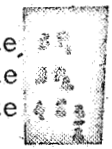
Page One Title  for the state 
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Muschlitz and Holt have used inhomogeneous fields to separate the metastable species of helium 2^3S which has a magnetic moment from the 2^1S type which does not have it.

HYDROGEN /14

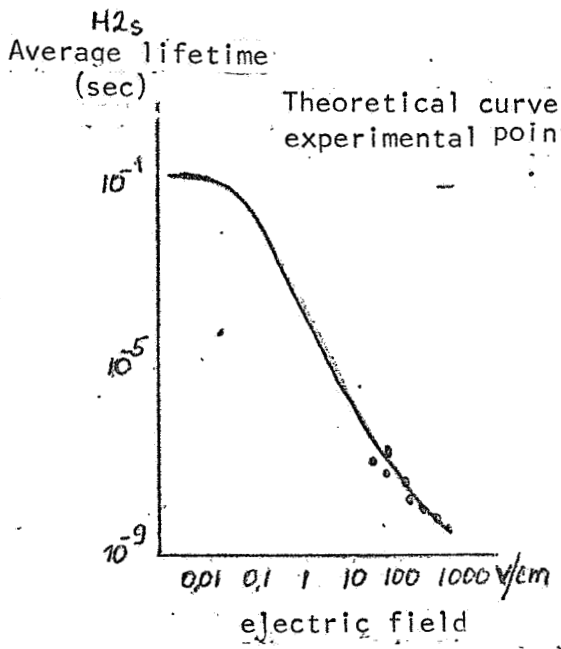


Figure 11-1 (JAECKS)

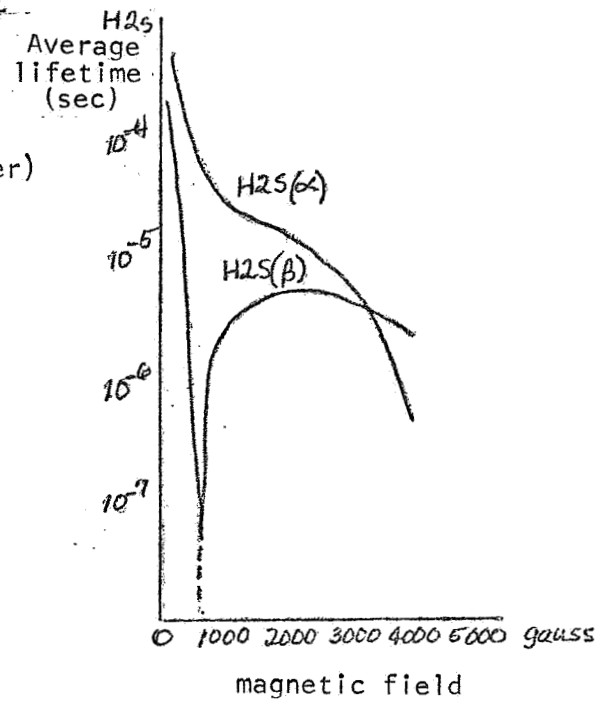


Figure 11-2 (LAMB)

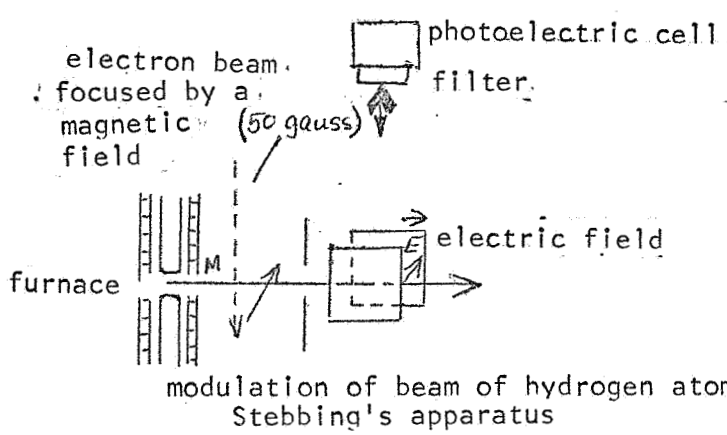


Figure 11-3

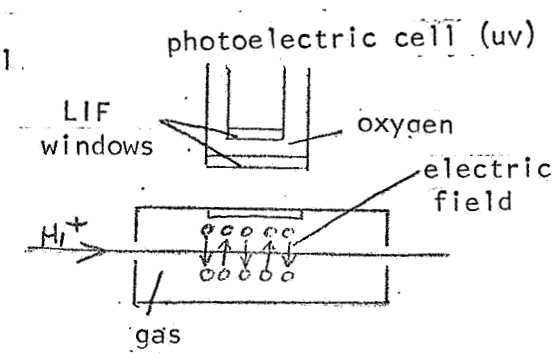


Figure 11-4

2) Impact of Metastable Particles on a Metal Surface: (SMITH-1955) KAMINSKY, 1965 /15

Page One Title

An atom which strikes a metal surface which is hot enough to reemit the atom, may give up an electron to the surface and be reemitted in the form of ions if the work function ϕ of the metal is higher than the ionization potential of the atom. If the atom is in a metastable state and if ϕ is lower than its internal energy, E_m, it could produce emission by the surface of an electron with a maximum energy $E_m - \phi$. This phenomenon occurs in the case of high temperature metastable species which strike a metal surface at ambiant temperature (ϕ is in the vicinity of 4 to 5 eV for W, Pt, Ar, Ni, Mo, and 2 to 3 eV for K, Na, C).

Is this a sub-heading?

a. Secondary electron emission is characterized by the coefficient γ_M which is the number of electrons emitted by metastable species. Account must be taken of emission of electrons by protons which are generally present at the same time. This can occur:

Cover Page Source

1) by placing a thin film of transparent collodion in the path of the photons,

2) by deflecting certain metastable species by means of an inhomogeneous magnetic field,

3) by rapid modulation of the metastable particles (so that the photons follow the modulation).

Value of experimental equipment and results.

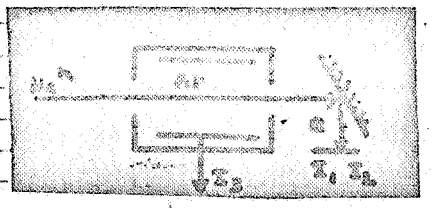
HELIUM He 2^3 S He 2^1 S

Dorrestein (1938) gives the first absolute values for Pt $\gamma_M(2^3S) = 0.24$, and $\gamma_M(2^1S) = 0.48$. These results are contested later on.

Schulz (1957) uses the value $\gamma_M(2^3S) = 0.29$ for gold according to Stebbing (not published).

Stebbing (1957) and Hasted (1959) measure $\gamma_M(2^3S)$ for Au, Mo, W, Pt, /16 sampling being made for Au. A beam of metastable particles passes through a chamber and strikes a gold target. The electron current is measured as $I_1 = I_M \gamma_M e$, I_M being the metastable flux and e the charge on the electron.

The argon is introduced into the chamber. A certain number of metastable species are destroyed by the reaction $He^M + Ar \rightarrow He + Ar^+ + e$ (Chapter III) and the electron current becomes $I_2 = I'_M \gamma_M e$. The number of metastable species



destroyed, $I_M - I'_M$, is given as the value of ion current Ar^+ $I_3 = (I_M - I'_M)\ e$, where $\gamma_M = \frac{I_1 - I_2}{I_3}$. In taking these measurements, Stebbing assumes that γ_M is the same for 2^3S and 2^1S.

	γ_M	γ'^*_M
Mo	0.19	0.11
W	0.17	0.19
Pt	0.26	0.25
Au	0.29 ± 0.03	

* These values correspond to surfaces cleaned electronically. γ'_M rapidly tends toward γ_M.

Muschlitz was lead to measure the ratio $\frac{\gamma_1 I_1}{\gamma_3 I_3}$ (γ_1 and γ_3 are the coefficients of $He2^1S$ and 2^3S). I_1 and I_3 are the values of metastable flux $He2^1S$ and 2^3S formed by diffusion of a gas that is bombarded with electrons Chapter I-1). In 1960, Muschlitz used the ratio x_1/x_3 given by Phelps and $\gamma_1/\gamma_3 = 2$ given by Dorrestein. In 1962, following observations by Stebbing and Phelps, he took $\gamma_1/\gamma_3 - 1$. In 1964 and 1965 he measured the ratio $\gamma_1 T_1/\gamma_3 T_3$ and the ratio I_1/I_3.

HYDROGEN H^2S /17

In 1950, Lamb expressed doubts about this method of detection by pointing out that 3.4 ev were enough to ionize H2S (10.2 eV). Therefore, it should be a matter of ionization of the metastable species (case $\phi > E_i$) rather than extraction of an electron from the surface. Nevertheless, he uses a value of 0.5 for γ_M for platinum (theoretical maximum value) in his preliminary calculations and then corrected by 1/80. He also assumes (in 1953) that γ_M is the same for Pt, W and Zr.

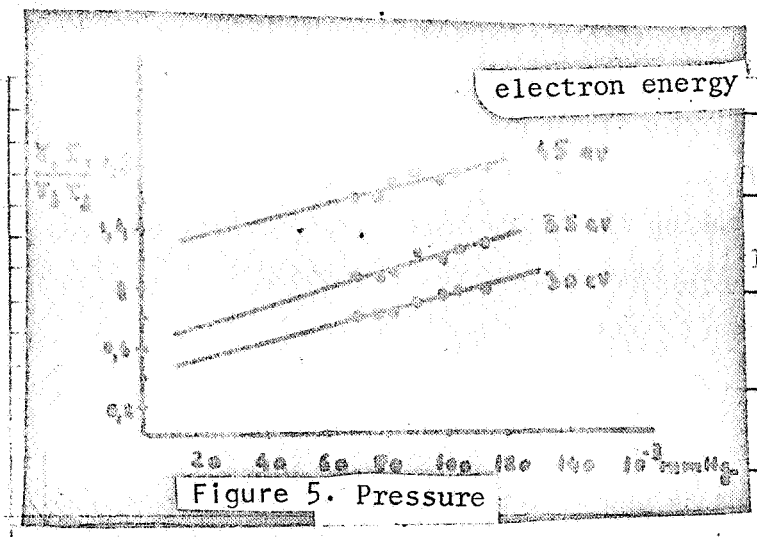


Figure 5. Pressure

I_1/I_3	Electron energy
0.29	30 eV
1	50 eV
2.4	140 eV

Heberle (1956) uses secondary electron emission of molybdenum, but does not give the value of γ_M. Lichten (1959) measures the coefficient γ_M for Pt. The method consists of destroying the metastable species by means of an electric field. The secondary electrons formed come only from the impact of the Lyman α photons emitted whose coefficient γ_p is known (0.018 ± 0.005). Taking into account the geometry of the apparatus, Lichten deduces the value $\gamma_M = 0.065 \pm 0.025$.

NEON-MERCURY-ARGON

Hasted (1959) (Neon), Lichten (1960), Sonkin, Webb, Couliette, Messanger (Mercury), and Muschlitz (1963)(Argon) used secondary electron emission to measure the metastable species of neon, mercury, and argon. Unfortunately they do not give the value of the coefficient γ_M used.

Molnar (Argon) evaluates γ_M at 0.023 for Ta and 0.065 for Mo.

3) Measurement of the Number of Electrons that Lose Energy

Should be in T.C.

/18

During the production of heated metastable particles by electron bombardment, energy is taken from the electron. Measurement of the number of these electrons will give the number of metastable particles formed.

HELIUM

Schulz (1959) has compared the results obtained by this method to those furnished by secondary electron emission by impact of metastable particles on a metal surface. The experimental apparatus is the same as that in Chapter I-1. Only the electrodes inside the collision chamber have been modified in such a way that the electron which has lost energy E_m in the inelastic collision with an atom can not leave the chamber and is captured by the anode M. An improved device consisting of two electrostatic analyzers at 127° was used by Schulz for the investigation of excited states, but not for the formation of metastable species.

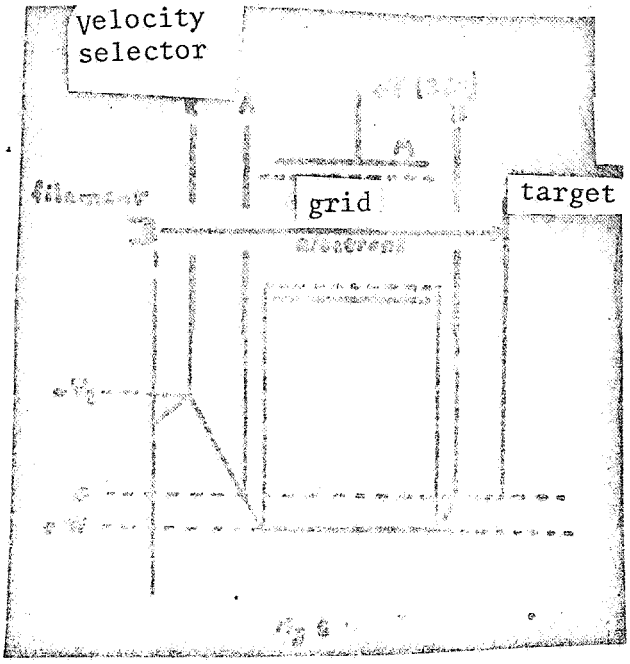


Figure 6.

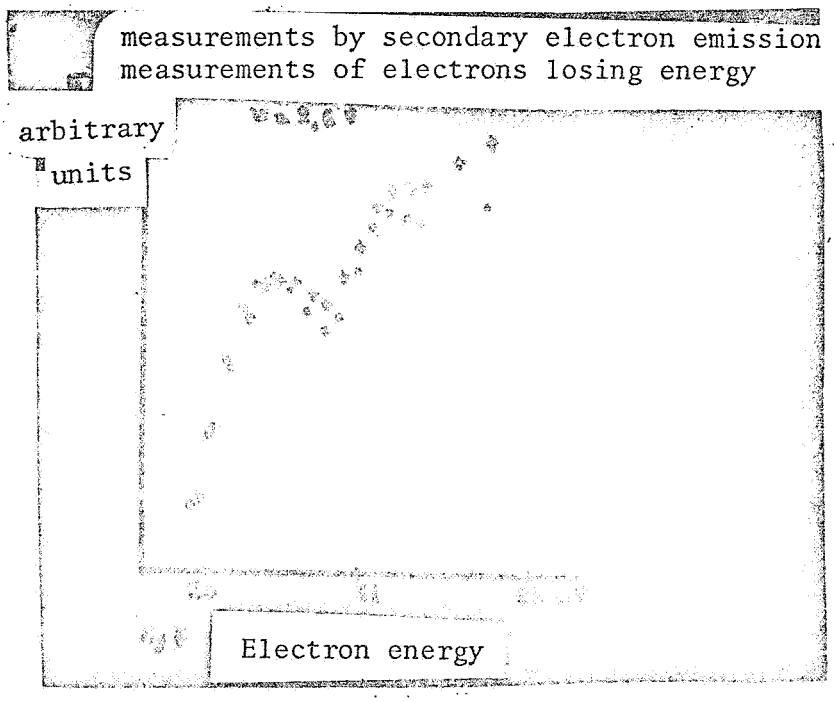


Figure 7.

Should be in T.C.

4) Absorption of a Light Ray

/19

The density of metastable species present in a gas may be deduced from the measurement of the absorption of a light ray of a certain wave length. The value of this wave length depends on the metastable species and on the measuring method used. For example, if the method uses a P.M., we must find a compromise between the value of the absorption coefficient of the ray and the spectro response of the P.M.

The absorption A is given by the relationship A = 1 - transmitted radiation/incident radiation.

$$A_\alpha = \frac{k_0 l}{\sqrt{1+\alpha^2}} - \frac{(k_0 l)^2}{2!\sqrt{1+2\alpha^2}} + \dots (-1)^{(n-1)} \frac{(k_0 l)^n}{n!\sqrt{1+n\alpha^2}} \quad (1)$$

(Mittchell pp. 118-322)

l being the thickness of the section of gas, k_0 the absorption coefficient at the center of the ray. $k_0 = \sigma N$ when the density N of the absorbing atoms is small. σ is a constant. α = emission band width/absorption band width. A_α is measured. We must know α and σ in order to obtain $N_0 = \frac{(k_0 l)}{\sigma l}$.

Determination of α: the curves in Figure II-9 represent $A_\alpha = f(k_0 l)$ for various values of α.

1) For low absorption, determination of the exact value is not necessary and will be taken to be equal to 1.

2) For high absorption, the value of α is determined by comparison between the experimental measurements of A_α for various values of l (the other parameters remaining constant) and the values of A_α obtained under the same conditions from relationship (1).

In general, $1 < \alpha < 2$.

Determination of σ: the value of the coefficient σ is obtained by calculation from the relationship

$$N_0 = \frac{2}{\sigma' l_0} \sqrt{\frac{\ln 2}{\pi}} \frac{\pi e^2}{mc} f_0 N = \sigma N \qquad \text{(Mittchell, p. 100)}$$

The experimenters use the theoretical results of Ladenburg and Damgaard-Bates to get the values of f. /20

Measurement Techniques.

The absorption is generally low (in the order of a few % for helium). It is therefore necessary to use difference or zero methods or modulation.

1) Modulation method, Phelps 1955-1959 (Figure II-10).

This device is widely used for the investigation of the variation of density of metastable particles, as a function of time, present in a pulse discharge. It results in the best signal to noise ratio.

2) Zero method.

Phelps (1953) measures the light intensity with absorption and then without absorption.

Smith (1963) uses a device which permits making simultaneous measurement (Figure II-2).

There is an advantage in using an intense light source in order to improve the signal to noise ratio, but it must be remembered that, in certain cases, the number of metastable particles destroyed may become large.

Experimental Investigations.

HELIUM

Phelps (1953-1955) and Benton (1962).

Wave lengths used: 10,830-3,889 for 2^3S
5,016 for 2^1S.

Value of α: 1.5 as determined by the variation of A_α as a function of 1.

Value of σ obtained by calculation from the work of Damgaard-Bates. /21

In the experiments performed by Benton, 1% of the absorption of the 3,889 corresponds to a density of $4 \cdot 10^9$ 2^3S metastable particles per cm^3 and 1% absorption of the 5,016 corresponds to a density of $1.4 10^9$ 2^1S metastable particles per cm^3.

NEON

Phelps (1953-1959), Dixon (1957), and Hadeishi (1962).

Wave lengths used: 5,945-5,882-6,143 for $3P_2$
6,266 for $3P_0$.

Phelps uses the relative absorption coefficients given by Shortley and takes α = to 1.6 and $\sigma = 7.6 \cdot 10^{-13} cm^2$ (5882) in order to obtain absolute values (calculation by Ladenburg: [illegible]).

Dixon determines α by means of the variation of the absorption length l and takes σ obtained by calculation from the work of Ladenburg.

Hadeishi takes α = to 1 and σ from the calculations by Damgaard-Bates.

[illegible]

Value of σ:

Wave Length	Dixon	Phelps
5 217	1.10^{-12} cm^2/atoms	
5 682	1,1 "	1 ($7,6.10^{-13}$ cm^2)
5 945	1,6 "	1,6
6 334	2,4 "	
6 143	3,9 "	
6 402	10 "	
6 266		14,3

MERCURY /22

Hadeishi (1965), Zemansky (1929-27) and Pool (1929).

Wave length used is 5,461 for $3P_2$ and 4, 047 for $3P_0$.

Value of α = 1.

ARGON

Molnar (1951) and Phelp (1953).

Wave length used 8,11 5 for $3P_2$.

KRYPTON

Smith (1963).

Wave length used 5,570 for $1S_5$.

CHAPTER III. PROPERTIES /23

1) General Considerations

Page One Title

The metastable particles are destroyed on the walls of the enclosure and by inelastic collisions with other particles, thus generating neutrons (excited or nonexcited), ions, electrons or photons.

Investigation of these collisions may be carried on by measuring the lifetime of the metastable particles present in a pulse discharge or by interaction of a beam of metastable particles with different media.

1) Measurement of lifetimes of metastable particles in a pulse discharge.

Should be in T.C

In a discharge there is equilibrium between the phenomena of formation and of destruction. At the instant that the discharge stops, most of the phenomena of formation disappear. The measurements of density are made at this moment.

Cover Page Source

The variation in density M, R, S, T, etc. of the metastable particles present as a function of temperature may be represented by the following types of relationships:

$$\frac{\partial H}{\partial t} = D_M \nabla^2 M - Q_{1M}(n_0, n_e, n_f, M, R, S \ldots) + Q_{2M}(n_0, n_e, n_f, M, R, S \ldots)$$

$$\frac{\partial R}{\partial t} = D_R \nabla^2 R - Q_{1R}(n_0, n_e, n_f, M, R, S \ldots) + Q_{2M}(n_0, n_e, n_f, M, R, S \ldots)$$

M_0, [illegible] and [illegible] being the densities of neutrons, electrons and impurities.

The first term represents diffusion due to elastic collision. This phenomenon is characterized by the diffusion coefficient D_m where D_0 ($D_0 = D_m/p$ p being the pressure) or by the effective diffusion cross section [illegible] (Massey, Burhop, p. 367).

The second term represents destruction of the metastable particles by inelastic collisions. This destruction generally takes place by:

a) collision with an atom (2-body collision) characterized by the coefficient A or an effective cross section σ_a defined by [illegible] /24

b) collisions with 2 atoms (3-body collision) characterized by the coefficient B

c) collisions with a metastable particle characterized by the coefficient α or the effective cross section σ_c defined by [illegible]

d) collisions with an electron characterized by the coefficient β or the effective cross section σ_d defined by [illegible]

e) collisions with another atom characterized by the coefficient A_1 or the effective cross section σ defined by [illegible], n_1 being the density of impurities.

Collisions with ions are neglected (considered theoretically by Allison).

Therefore, Q_1 will generally be in the form

[illegible]

or

[illegible]

The third term Q_{2M} represents the formation of the metastable species of type M through inelastic collision. Generally, this formation takes place:

a) by collision with an electron, characterized by the coefficient β'

b) by collision of an excited or metastable atom with another atom, characterized by the coefficient A'.

Therefore, Q_2 will generally be of the form

[illegible]

N being the density of atoms in an excited state.

The principle of the method consists in experimentally measuring the function M(t), R(t), S(t), etc., under special experimental conditions which permit the simplifications required for solving equation /25

$$\frac{\partial H}{\partial t}, \frac{\partial R}{\partial t}, \frac{\partial S}{\partial x}$$

etc. Comparison of the functions obtained, M(t), R(t), etc., with those measured permits determining the coefficient A, B, α, etc.

2) Measurent of Products of Reactions Formed by Passing a Beam of Metastable Particles Through Various Media Should be in TOC

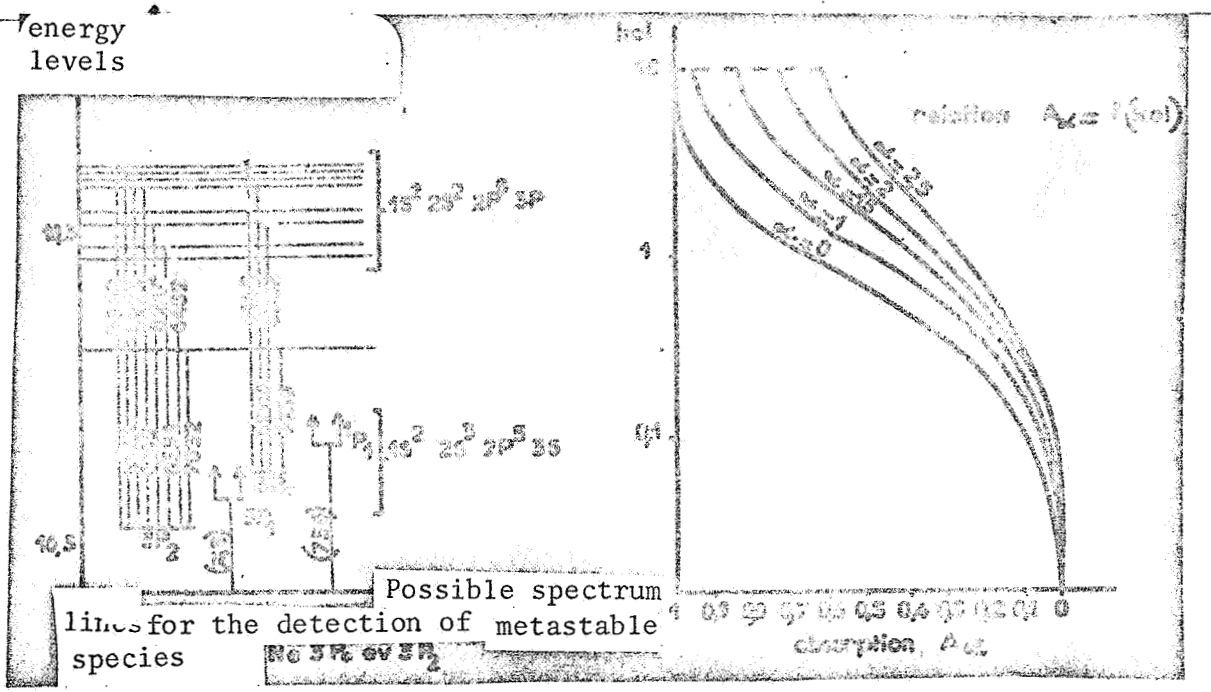


Figure II-8 (Dixon)

Figure II-9 (Dixon)

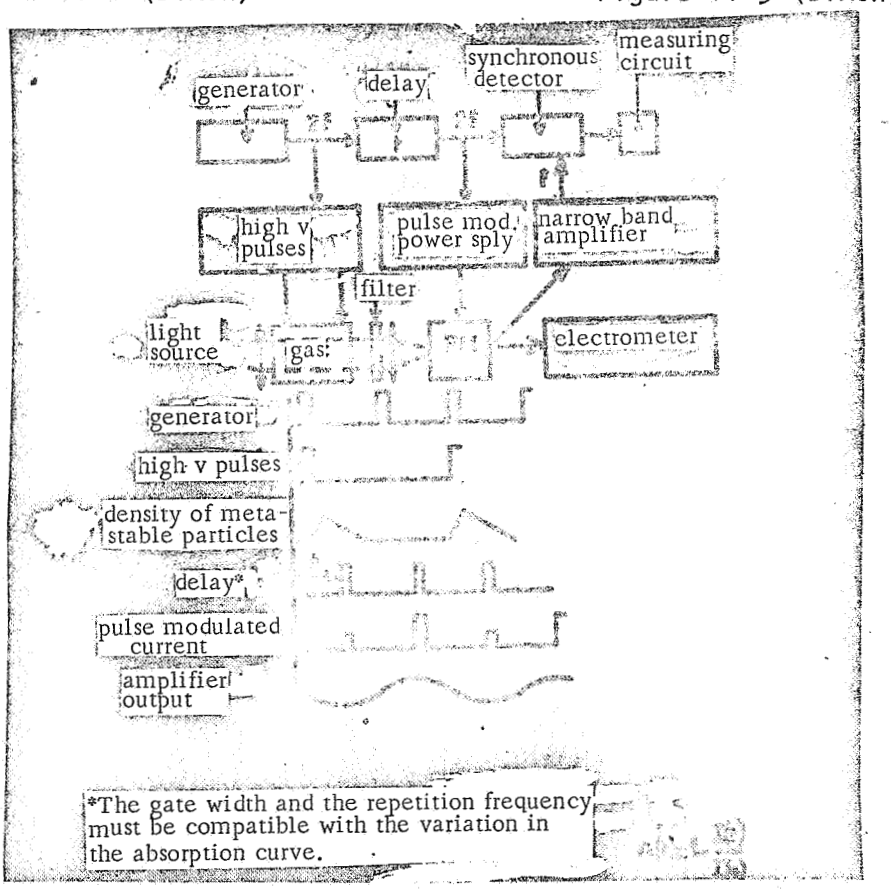


Figure II-10 (Apparatus Used by Phelps)

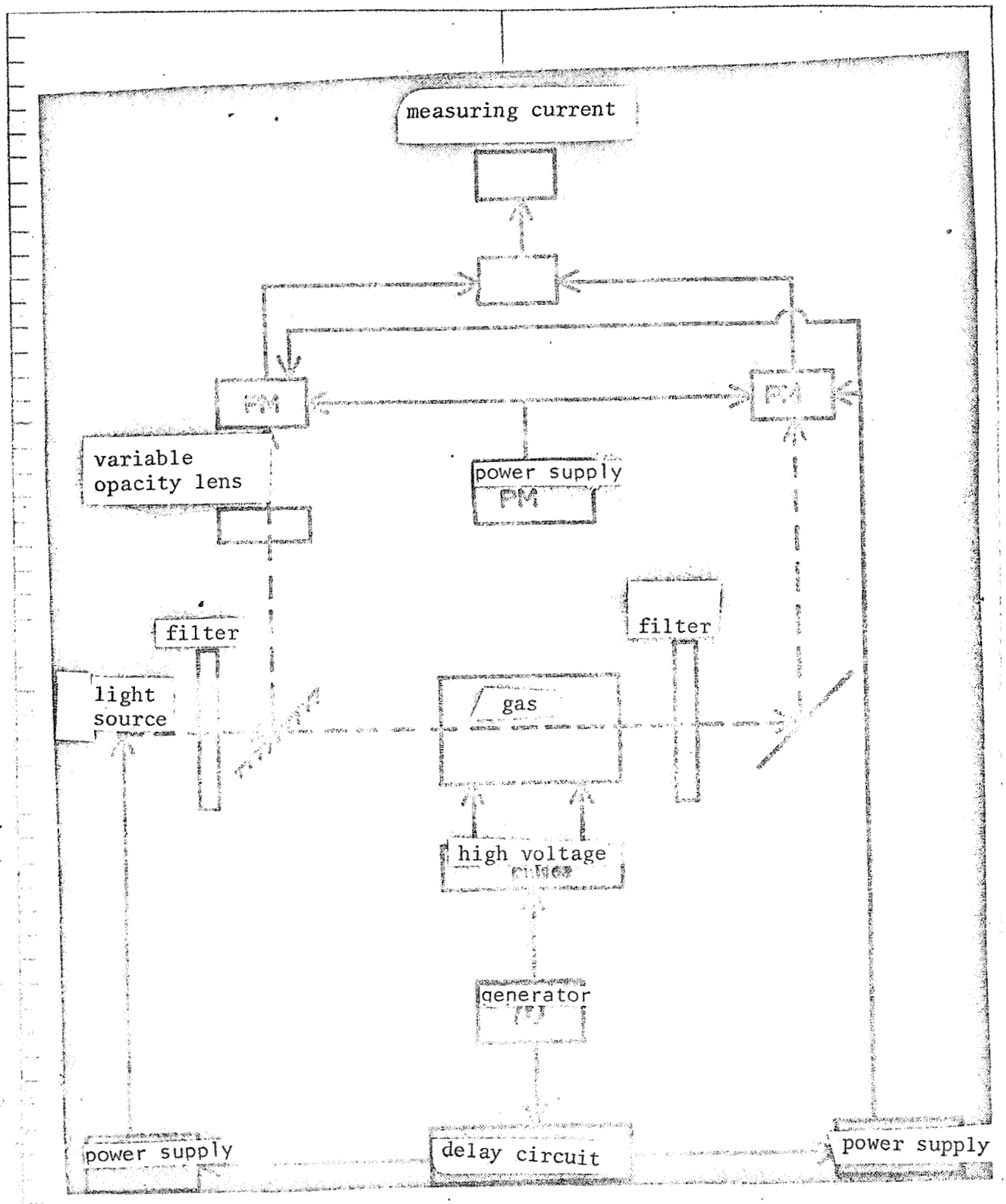


Figure II-11 (Apparatus Used by Smith)

Given a beam of metastable particles of flux I_0 traveling over a length 1 in a medium of density n. The number of particles I_j formed by a given reaction will be given by the relationship $I_j = I_0 (1 - \exp - \sigma_j n l)$, σ_j being the effective cross section characterizing the given reaction. Measurement of I_j, I_0, n, and 1 permit determination of this effective cross section.

Remarks--the beam may be formed of metastable particles of different types (generally two). The effective cross section defined above will then be an average effective cross section $\bar{\sigma}_j$ in the case of two types of metastable particles $\bar{\sigma}_j = \frac{\sigma_{j1} I_{01} + \sigma_{j2} I_{02}}{I_{01} + I_{02}}$, I_{01}, I_{02} being the flux of the metastable particles of types 1 and 2 and σ_{j1}, σ_{j2} the effective cross sections for process j of metastable particles of types 1 and 2. In the case of beings of heated metastable particles, it may be necessary to take into account the velocity of the target particles (cf. Chapter II-b).

Experimental Results

HELIUM

/26

2^1S and 2^3S metastable particles.

Is this a sub-title?

Collisions Investigated Which Lead to the Destruction of Metastable Particles.

a) 2 body collision. $He^m + He \rightarrow He_2$ the molecule which is formed has a rather long lifetime. The 2 body collision has been studied by Nikerson (1935).

b) 3 body collision. $He^m + 2He \rightarrow He_2 + He$ the 3 body collision has been studied by Meyerott (1949) and Phelps (1955) (Figure III-1).

c) Collisions between metastable particles. $He^m + He^m \rightarrow He^+ + He + e$.

d) Collision with an electron. $He2^1S + e \rightarrow He2^3S + e$. The heating of electrons by these reactions has been studied by Imgraham (1963).

e) Collision with an electron. $He^m + e \rightarrow He^+ + 2e$.

f) Collision with an atom. $He^m + X \rightarrow X^+ + He + e$. This reaction which is called the "Penning ionization" takes place if the ionization potential of X is lower than the internal energy of the heated metastable particles He^m (studied by Ferguson 1962).

Is this a sub title?

Collisions Investiged Which Lead to the Formation of Metastable Particles.

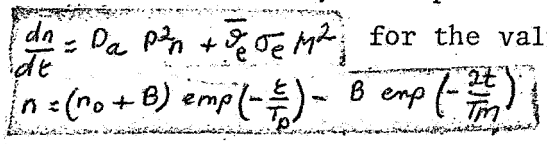
a) Electron collision. $He2^1S + e \rightarrow He2^3S + e$.

Biondi (1951-52) studies the variation in density of a mixture of 2^1S and

2^3S metastable particles in a pulse discharge in pure helium and in the presence of impurities.

Pure Helium. Biondi assumes the relationship  . Assuming a fundamental mode of diffusion, integration of the preceding equation gives  , the diffusion length  for a cylinder of length L and radius R. When multiplied by the pressure p, $1/T_m$ gives the relationship  . Investigation of the variation of p/T_m as a function of p^2 gives the value of D_0 and A, and therefore of σ_a.

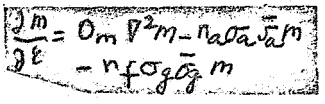
Measurement of $1/T_m$ and of Mo for a given pressure p. Biondi assumes that /27 the electron density n in pure helium is governed only by the reaction (c)

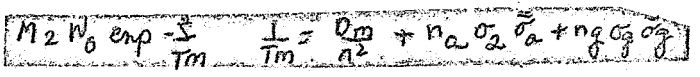


for the value of M(t) 

The density n(t) is measured experimentally by means of micro-waves (Figure III-2). The straight portion at T, represents the first term of the equation n(t), the metastable particles having been destroyed. The difference an obtained between the measured value and the extrapolated value of the right side represents the second term of the equation. The slope of this straight line gives the value of Tm and the ordinate for the zero value of t gives that of B, therefore the value of Mo. By substituting for σ_c the value Phelps used, 10^{-14} cm^2, Mo = $5 \cdot 10^{10}$ p/cm^3 (at a pressure of helium of 2.5 mm Hg). The variation of p/T_m as a function of p^2 (Figure III-3) gives the values of Dm and σ_a. ($D_m p = D_0$) diffusion: D_0 = 520 ± 20 cm^2/sec. (mm Hg), 2 body collision: $\sigma_a = 9.6 \cdot 10^{-21}$ cm^2.

Presence of impurities (Ar and Hg). Biondi assumes the relationship





therefore by multiplying the pressure p,  investigation of the variation of p/T_m as a function p gives the value of $A + A_1$, and since A has been previously determined, the value of A_1 is therefore σ_f.

Measurement of $1/T_m$ for a given pressure p. Biondi assumes that in the presence of impurities in sufficient quantity (0.1 to 0.2%), the electron density n is governed by the reaction f. Therefore $\frac{dn}{dt} = \frac{D'}{a} p^2 n + n f \sigma_f \bar{v}_f m_1$

$$n = (n_0 + B') \exp\left(-\frac{t}{T_m}\right) = B' \exp\left(-\frac{t}{T_m}\right) \qquad B' = \frac{n f \bar{v}_f \sigma_f m_1}{\frac{1}{T_m} - \frac{1}{T_0'}} \qquad \frac{1}{T_0'} = \frac{A^2}{D_2'}$$

T_m and B' are determined as previously. Mo = $2.5 \cdot 10^{10}$ p/cm^3 at a pressure of helium of 2 mm Hg; collision with impurities; $\sigma_f = 9.7 \cdot 10^{-17}$ for argon; $\sigma_f = 1.4 \cdot 10^{-14}$ for mercury.

HELIUM (Continued) /28

Phelps (1953-1955) investigated the variation of density of metastable states 2^3S and 2^1S separately in a pulse discharge in pure helium and in the presence of impurities.

Pure helium and low density of metastable particles; Phelps assumes the set of equations:

$$\frac{\partial S}{\partial t} = D_S \nabla^2 S - A p S + \beta n_e S \qquad \text{S is the density of } 2^1S \text{ helium}$$

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T - B p^2 T + \beta n_e S \qquad \text{T is the density of } 2^2S \text{ helium.}$$

He assumes a fundamental mode of diffusion and that the electron density remains constant over time and space during the time necessary for the destruction of a singlet. This last hypothesis has been verified experimentally, since the lifetime of the singlet is less than that of the triplet. With these hypothesis, the set of equations becomes:

$$S_z S_0 e^{-\gamma_S \tau} \qquad \gamma_S = \frac{D_S}{\Lambda^2} + A p + B n_e$$

$$T_s (T_0 + T_S) e^{-\gamma_T t} - T_S e^{-\gamma_S \tau} \qquad \gamma_T = \frac{D_T}{\Lambda^2} + B p^2 \,, \quad T_S = \beta n_e S_0 (\gamma_3 - \gamma_n)^{-2}$$

Measurements of the absorption of the spectrum line permit obtaining the values S(t) and T(t) (Figure III-4). The comparison of these results with the functions S(t) and T(t) give the values of γ_S and γ_r for a given pressure p and electron density n_e. Curve $\gamma_S(n_e)$ as a function of electron density n_e (Figure III-5) gives the value of p and therefore of σ_α. Curves $\gamma_S(p)$ and

$\gamma_T(p)$ as a function of pressure p (Figure III-6) gives the values of the coefficients D_S, D_T, A and B.

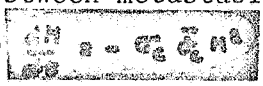
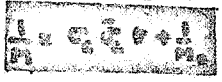
coefficient of diffusion	$He2^1S$	$D_S = 440 \pm 50$ cm^2/sec. (for 1 mm Hg)
	$He2^3S$	$D_T = 470 \pm 25$ cm^2/sec. (for 1 mm Hg)
3 body collison	$He2^3S$	$B_T = 0.21$ sec^{-1} mm^{-1}
2 body collision	$He2^1S$	$\sigma_\alpha(S) = 3 \cdot 10^{-20}$ cm^2
2 body collision	$He2^3S$	$\sigma_\alpha(T) = 10^{-22}$ cm^2
electron collision		$\sigma_\alpha = 3 \cdot 10^{-14}$ cm^2

/29

($He2^1S + e \rightarrow He2^3S + e$)

(the value $\sigma_\alpha(T)$ measured by Phelps in 1953 justifies suppression of the 2 body collision term in the relationship dealing with the triplet).

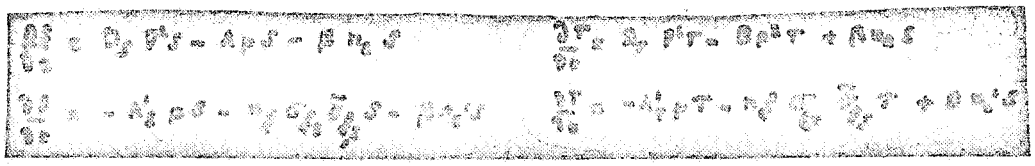
Pure Helium and High Density of Metastable Particles.
Is this a sub-title?

Phelps assumes thst under certain conditions, which he does not specify, collisions between metastable particles play a leading role. He assumes the relationship  or  . Measurement of the density of metastable particles by means of absorption of a spectrum line gives the values of M(t) (Figure III-7) while the slope of the linear portion gives the value of σ_e:

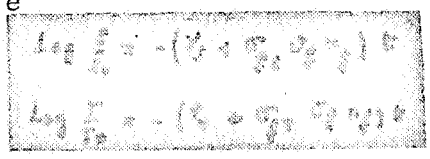
collision between metastables $\sigma_e = 10^{-14}$ cm^2.

Presence of impurities: Phelps (1953) points out the influence of the presence of argon. He assigns the value of σ_f but does not specify the method of measurement. [$\sigma_f = 3 \cdot 10^{-17}$ cm^2 for Ar.]

Benton (1962) measures the effective cross sections of destruction of the singlets and triplets by impurities Ar, Kr, Xe, N_2, He, Ne. The relationships are:



by neglecting the terms βn_e'S



Benton measures coefficients D_T, B, and effective cross section σ_f by comparing the slopes of the linear portions of curves M(t) which are obtained experimentally (Figure III-8) by absorption of the spectrum line in pure helium and in helium containing impurities. Unfortunately, he does not give any details about his measurement methods. Specifically, he does not mention whether the coefficient β was measured or was assumed. /30

diffusion of the triplet $D_T = 560 \pm 50$ cm^2/sec (at 1 mm Hg)

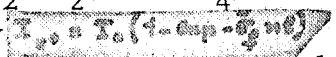
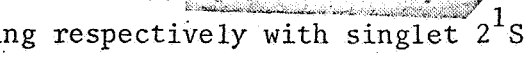
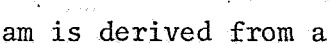
3 body collision (2^3S) $B_T = 0.31 \pm 0.03$ sec.$^{-1}$ mm^{-2}

value of σ_f Ar, Kr, Xe, N_2, He, Ne (cf. Table V-2).

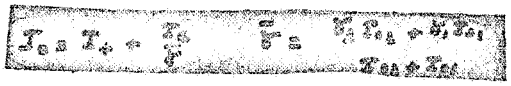
Effective Cross Sections σ_f (cm^2) for the Reaction $He^m + X \rightarrow He + X^+ + e$

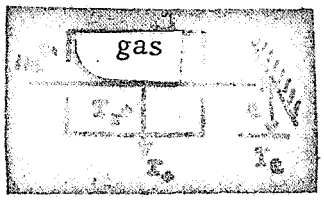
He^m	Oianoi		Benton		Muschlitz	
	2^1S	2^3S	2^1S	2^3S	2^1S	2^3S
Ar						
Kr						
Xe						
N_2						
CO						
NO						
O_2						
C_2H_2						
H_2						

/3

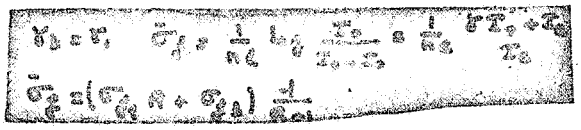
Muschlitz (1962-1963) measures the effective cross sections σ_f for the reactions $He^m + X \rightarrow He + X^+$ produced by a beam of heated metastable particles passing through Ar, Kr, Xe, H_2O_2, N_2, CO, CH_4, and C_2H_6. The average effective cross section $\bar{\sigma}_f$ is defined by  and  ,  dealing respectively with singlet 2^1S and triplet 2^3S. Since the beam is derived from a gas that is excited by electrons, the ratio 

depends on the gas pressure and the energy of the electrons. The beam of metastable particles is measured by secondary electron emission:





Like Stebbing, Muschlitz assumes that



the value of  as a function of R gives the values σ_{f1} and σ_{f3}.

Fite (1963) measures the effective cross section σ_e for the reaction $He^m + e \rightarrow He^+ + 2e$. The beam of metastable particles obtained by diffusion from an HF source is formed of a mixture of 2^1S and 2^3S. It is bombarded at the right angles by a beam of electrons with a variable energy (10 to 24 eV). The ions formed are separated from the beam of neutral particles by a magnetic field and measured at a target. The metastable particles are measured by secondary electron emission. The maximum value is $\sigma_e = 2.8 \cdot 10^{-16}$ cm^2 for electrons of 13 eV, (the maximum ionization effective cross section of helium in the fundamental state is $\sigma_i = 0.35 \cdot 10^{1-6}$ cm^2 for electrons from 130 to 115 eV).

Stebbing (1957) and Hasted (1959) measure the total effective cross section of the absorption of a beam of heated metastable particles passing through various gases. The diffusion coefficient for this effective cross section is called D_m.

The beam of flux I_0 travels length Z in a medium of density n. The remaining flux I_1 impinges on a target where it is measured by secondary electron emission. The effective cross section σ_t is given by the relationship /32

$I_1 = I_0 \exp(-\sigma_t n \ell)$ $\log I_1 = \alpha + \beta \sigma_t p$, p being the pressure. The measurement I_1 (p) gives the value of σ_t.

The accuracy of measurement depends on the angle of resolution of the apparatus. Willmore, in a private communication, indicates that in the case of helium, an angle of resolution of 1° produces an error less an 6%.

The influence of the photons present in the beam of metastable particles is evaluated by interposing a collodion film (Stebbing) or by modulation (Hasted).

Stebbing and Hasted believe that the beam used is formed only by triplet 2^3S.

$He 2^3S$	$He\ 10^{-16}\ cm^2$	Ne	Ar	Kr	Angle of Resolution
Stebbings	149	119	211	418	2°
Hasted (1)	145	127	200		0.1 at 1°
Hasted (2)	109	116	188		Values corrected in 1964

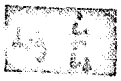
(2) Hasted (1964) corrected his values in order to take into account the relative velocities of the incident particles and the particles striking the targets and to obtain a better estimate of the density of the gas.

Muschlitz (1962-1964) measures the total effective cross sections of absorption of a beam of metastable particles traversing various gases as a function of the angle of resolution.

The beam is formed of singlet I_{01} and triplet I_{03}. The effective cross sections are defined by equations $I_1 = I_{01} \exp(-\sigma_1 n \ell)$ $I_3 = I_{03} \exp(-\sigma_3 n \ell)$ /33
The flux of metastable particles is measured by secondary electron emission.

$I_1 = \gamma_1 I_{01} + \delta_1 I_{03}$ $I_2 = \gamma_2 I_{01} + \delta_2 I_{03}$

$\frac{I_2}{I_1} = \frac{\gamma_2 + \delta_2 \exp(-\sigma_3 n \ell)}{\gamma_1 + \delta_1 \exp(-\sigma_3 n \ell)}$ $\alpha = \frac{\gamma_1 \gamma_2}{\delta_1 \delta_2}$ $\frac{I_2}{I_1} = \frac{\sigma_1 + \alpha \sigma_3}{1 + \alpha}$ $n \ell$

Measurement of  as a function of pressure p, for a given value of R, gives the value of

The values of m/e as a function of 1/1 + R gives σ_{t3} for 1/1 + R = 0 and σ_{t1} for 1/1 + R = 1.

Since the target particles do not all have the same speed and since these speeds are not negligible compared to those of the metastable particles, the total absorption effective cross section is an average value Q that is related to the effective cross section σ by a coefficient which depends on the masses and the velocities of the particles.

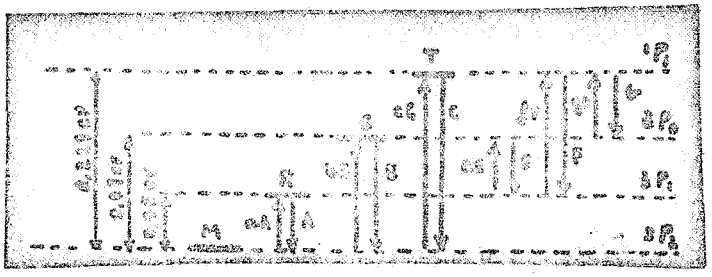
$\phi = 0.766\ \sigma$ for helium. $\phi = 0.916\ \sigma$ for neon.

Angle of Resolution	Helium 300° K $3 \cdot 10^{-16}$ cm^2		Neon 300° K $3 \cdot 10^{-16}$ cm^2		Argon 10^{-16} cm^2
1° 22'	75 ± 5	41 ± 4	74 ± 5	29 ± 3	
3°	52 ± 4	31 ± 4	50 ± 4	19 ± 3	
5°	42 ± 4	26 ± 4	40 ± 4	15 ± 3	
8° 21'	40 ± 4	26 ± 4	40 ± 4	17 ± 3	39 ± 5 / 51 / 8 cm
8° 53'	32 ± 4	23 ± 3	37 ± 4	15 ± 3	

The total absorption effective cross section represents the effective cross section of elastic collision, since the loss of particles by inelastic collision is generally negligible (the effective cross sections for the inelastic process varies from 10^{-20} cm^2 to 10^{-16} cm^2). Only reactions of the type $He^m + He \rightarrow He + He^m$ (exchange of excitation) and certain ionization reactions ($He^m + X \rightarrow He + X^+ + e$) have effective cross sections close to 10^{-15} ($7 \cdot 10^{-16}$ for the first one evaluated by Muschlitz, and 6 to $7 \cdot 10^{-6}$ for the second in the case of argon). However, measurement of the ions formed permits taking into account the loss of metastable particles through this reaction. /34

Metastable particles $3P_2$, $3P_0$.

The presence of four very close levels $3P_2$, $3P_1$, $3P_0$, $1P_1$ of the configuration $1s^2 2s^2 2p^5 3s$ makes the investigation of collisions of metastable particles with neon more complex than that with helium, since each of these states can collide with an atom or an electron and generate three others. Therefore, there are twelve possible reactions represented by coefficients A, B, C, D, E, F, G and aA, bB, cC, eE, fF, gG, but some of them are not important.



Experimental Investigation

1) Collisions investigated involving the destruction of metastable particles $3P_2$ amd $3P_0$.

a) 2 body collision: the metastable species $3P_0$ may generate an excited state or a metastable species $3P_0 \rightarrow 3P_1$

$$3P_0 \rightarrow 3P_2$$

b) 3 body collision

c) collision with an electron $3P_0 + e \rightarrow 3P_1 + e$

d) with another atom, $Ne^m + X \rightarrow Ne + X^+ + e$ if the ionization energy of X is less than the internal energy of Ne^m.

2) Collisions investigated involving the formation of metastable species $3P_2$.

a) 2 body collision: $3P_1 \rightarrow 3P_2$

$3P_0 \rightarrow 3P_2$

b) collision with an electron $3P_1 + e \rightarrow 3P_2 + e$

Zemansky (1929), Biondi (1951-52), and Phelps (1953) investigated the collisions of a mixture of $3P_2$ and $3P_0$ of neon in a pulse discharge without taking into account the particular reactions produced by the four very /36

adjacent levels. Their method of measurement is identical to that used by them for helium. Zamansky and Biondi used the equation

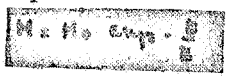
(Figure III-9) and Phelps the equation

Results: $\sigma_a = 8.9 \cdot 10^{-20}$ cm^2

$\sigma_f = 2.6 \cdot 10^{-14}$ cm^2 (Argon)

Do = 150 cm^2 sec^{-1}	Do = 60 cm^2 sec^{-1}
A = 50 sec^{-1} mm^{-1} } at 300° K	A = 0 } at 77° K
B = 0	B = $5 \cdot 10^{-2}$ sec^{-1} mm^2

Dixon (1957) investigated the collisions of metastable particles $3P_2$ and $3P_0$ in a pulse discharge in pure neon and in a mixture of neon and helium.



The density of each state $3P_2$ and $3P_0$ as a function of time is measured by the absorption of a spectrum line of light.

This measurement determines the value of t for a given pressure. The variation of 1/t as a function of p permits obtaining D_0 and A (Figure III-10).

Pure neon: $3P_0$ {Do = 170 cm^2 sec^{-1} ± 10 ($\sigma = 42.7 \cdot 10^{-16}$ cm^2)

{2 body collision $\sigma_a = 10.4 \cdot 10^{-20}$ cm^2

$3P_2$ {Do = 170 cm^2 sec^{-1} ±10 ($\sigma = 42.7 \cdot 10^{-16}$ cm^2).

Mixture of neon and helium. Dixon assumes that the equations used in the case of pure neon are also valid here.

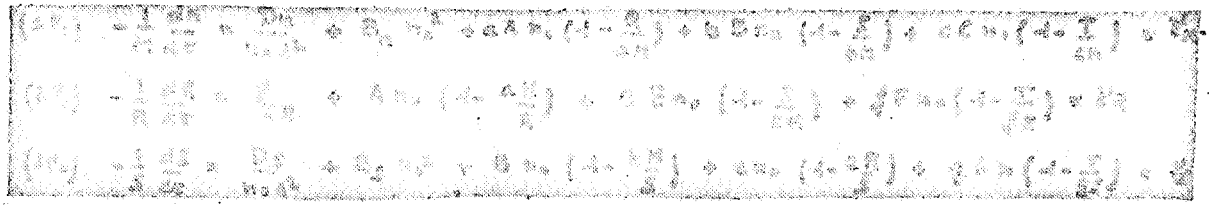
$3P_0$ {Do = 310 ± 20 cm^2 sec^{-1} ± 20 ($\sigma = 40.5 \cdot 10^{-16}$ cm^2)

{2 body collision $\sigma_a = 6.1 \cdot 10^{-20}$ cm^2

$3P_2$ {Do = 310 ± 20 cm^2 sec^{-1} ± 20 ($\sigma = 40.5 \cdot 10^{-16}$ cm^2)

Phelps (1959) takes up Dixon's measurements. He assumes that the metastable particles are destroyed by 2 and 3 body collisions and that some of these reactions produce metastable particles and excited states which may in turn produce reactions.

By assuming a fundamental mode of diffusion and by neglecting collisions between metastable particles and electrons, he obtains the following set of equations:

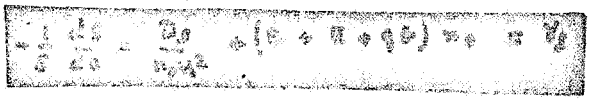


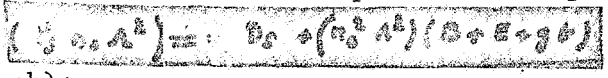
M, R, S, and T are the densities of states $3P_2$, $3P_1$, $3P_0$, $1P_1$. a, b, c, e, f, g, A, B, C, E, F, G are coefficients that characterize the twelve reactions among the four states. γ_{IR} is the attenuation constant for the radiation of entrapped resonance. a, b, c, e, f, and g are known (Schultz-Shortley). γ_{IR} has been calculated by Holstein. A, B, C, E, F, and G are unknown and must be measured.

Investigation of metastable species $3P_0$:

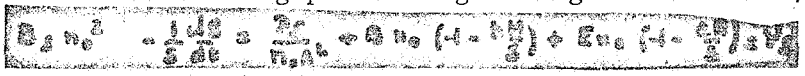
Experimental investigation for small values of time (Figure III-11) and the values of coefficients a-g permit neglecting the terms  .

By neglecting the term $B_S n_0^2$, we obtain: 



Absorption measurement of a spectrum line gives the value of γ_s and the variation of  results in values for D_S and (B + E + gb): /38

$D_S = 5.8 \cdot 10^{18}$ cm^{-1} sec^{-1} $\qquad$ $B + E + gb = 8 \cdot 10^{-15}$ cm^2

Experimental investigation for large values of time t and values of  coefficients a-g permit neglecting the term  Measurement of densities M(t) R(r) and S(r) permits obtaining the value of ratios R/S and H/S and the value of γ_S for a given pressure. The variation of  =  as a function of  gives the values of B and E, consequently of σ.

2 body collision $3P_0 \rightarrow 3P_1$ ($B = 5 \cdot 10^{-15}$ cm^3/sec) $\sigma_a = 6 \cdot 10^{-20}$ cm^2

$3P_0 \rightarrow 3P_2$ ($E = 5 \cdot 10^{-15}$ cm^3/sec) $\sigma_a = 6 \cdot 10^{-20}$ cm^2

Investigation of metastable species $3P_2$.

As in the case of the $3P_0$ species, the term S/bM and T/en are neglected. Therefore,  γ_M is determined by absorption measurements of the spectrum line of light.

For low density, the variation of [illegible] as a function of [illegible] results in the value of $D_M = 5 \cdot 10^{18}$ cm^{-1} sec^{-1}. For high density; the variation of [illegible] as a function of [illegible] gives the values of A and B_M.

2 body collision: $3P_1 \rightarrow 3P_2$ ($A = 4.1 \cdot 10^{-14}$ cm^3/sec) $\sigma_a = 5.2 \cdot 10^{-19}$ cm^2. /3

3 body collision: $B_M = 0.5$ sec^{-1} mm (300°K).

Electronic Collisions

To the relationships [illegible] must be added terms of the form [illegible], n_e being the electron density.

By using Dixon's results obtained with a pulse discharge (30 mA) and by considering only the reaction $3P_1 + e \rightarrow 3P_2 + e$ and $3P_0 + e \rightarrow 3P_1 + e$, while neglecting the others, Phelps evaluates the effective cross section σ_α:

$\sigma_\alpha = 10^{-13}$ cm^2 for $3P_1 \rightarrow 3P_2$ (for heated electrons)
$\sigma_\alpha = 10^{-14}$ cm^2 for $3P_0 \rightarrow 3P_1$

Hasted (1959), proceeding exactly as for helium, measured the total absorption effective cross section of a beam of metastable neon traversing various gases: helium, neon, and argon.

Ne^m	[illegible]	[illegible]	[illegible]	Angle of Resolution
[illegible] (1959)	206	153	278	1°
[illegible] (1964)	92	112	338	1°

* Corrected values which take into account velocities of target and incident particles and are a bare estimate of the gas density.

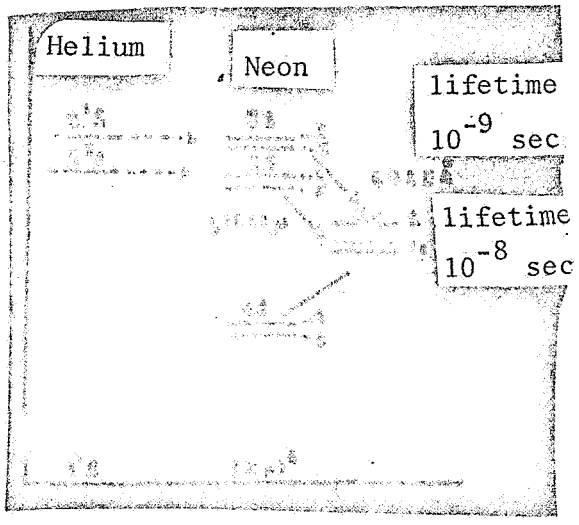
Muschlitz (1963), proceeding exactly as for helium, measures the effective /40 cross sections for the reaction $Ne^m + X \rightarrow Ne + X^+$, the target being CH_4 for C_2H_6.

	100	65	5

	10	33	100	36	31	11

Mixture of Helium and Neon

When a metastable particle with a thermal energy O^m meets an atom X, reaction $O^m + X \rightarrow X^+ + O + e$ takes place if the excitation energy of O^m is greater than the ionization energy of X^+. Reactions of this type can not occur for a discharge in a mixture of helium and neon. (Ne^+ = 21.56 eV, He^+ = 24.58 eV, He^m = 20.55 eV, Ne^m = 16.62 eV). A destruction mechanism of metastable particles He^m in neon were studied by Suzuki (1964) and Pariser (1965) in connection with the operation of neon-helium gas lasers.



The metastable particles 2^1S and 2^3S present in a neon-helium discharge permit the passage, by means of inelastic collision, of atoms of neon in the excited states 2^3S and 2^1S which destroy themselves while emitting spectrum lines 6,328 Å units and 1.1523 μ.

Since the lifetime of the metastable particle 2^3S is longer than that of 2^1S, the intensity of spectrum line 1.1523 μ is greater than that of the 6,328 Å line.

Argon, metable species $3P_2$. /41

Phelps (1953) studied the collisions experienced by the metastable species $3P_2$ present in a pulse discharge in argon in the presence of impurities exactly as in the case of helium in pure argon. He used an equation [illegible]. Measurement of the density M(r) for absorption of a spectrum line of light gave the value of the coefficients:

$D_0 = 54\ cm^2\ sec^{-1}$ $A = 40\ sec^{-1}\ mm^{-1}$ $B = 9\ sec^{-1}\ mm^{-2}$ (at 300°K)

(The values at 77° K are not reproducible). In the presence of impurities (Hg, Kr, H_2), Phelps gives the effective cross sections of the destruction of the metastable species $3P_2$ without giving details of the method used.

$\sigma_f = 3 \cdot 10^{-15}$ cm^2 (Hg)
$\sigma_f = 10^{-16}$ cm^2 (Kr)
$\sigma_f = 3 \cdot 10^{-17}$ cm^2 (H_2)

Muschlitz (1963), using an identical method as that for measuring helium, obtained the effective cross sections for the reactions

$$Ar^m + C_2H_6 \rightarrow Ar + X^+$$

Formed ions	$C_2H_6^+$	$C_2H_4^+$
$\sigma(10^{-16}\ cm^2)$	90	100

Mercury, metastable species $3P_0$. /4

Webb (1924-1929) and Coulliette (1928) studied the diffusion of metastable $3P_0$ produced by electron bombardment of mercury vapor.

Zemansky (1927-1929) and Samson (1932) showed that this metastable species could be produced under other conditions. Thus, the mercury vapor or better yet the mixture (Hg-N_2) irradiated by spectrum line 2,537 continues to emit this line after the excitation is eliminated. They assumed that this phenomenon was due to the presence of the metastable state $3P_0$(4.66eV) which, by means of collision, creates $3P_1$(4.86eV) in the excited state, emitting the 2,537 Å line.

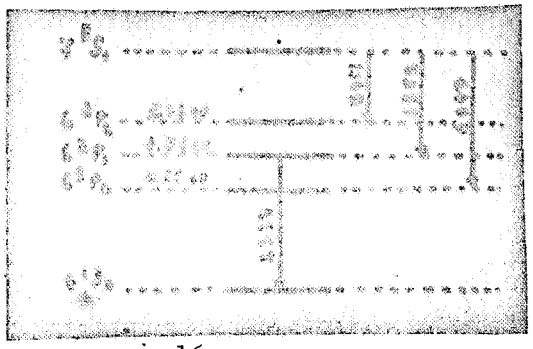
The densities of excited states $3P_1$ and $3P_0$ may be represented by equations of the same type as those used by Phelps in 1959 for neon.

Zemansky and Samson assumed that the most important inelastic collisions are those which involve 2 bodies as follows:

$3P_0$ + neutral particle (Hg or N_2) → $3P_1$
$3P_0$ + neutral particle → 1So
$3P_1$ + neutral particle → $3P_0$
$3P_1$ + neutral particle → 1So

based on this hypothesis, the equations [illegible] yield the functions

M(t) and R(t). Measurement of the decrease in intensity of the 2,537 Å line permits calculation of the values of effective cross section for diffusion and for 2 body collisions.



σ (by diffusion) $= 15.6 \cdot 10^{-16}$ (301°K) /43

$= 17.7 \cdot 10^{-16}$ (374°K)

$= 18.4 \cdot 10^{-16}$ (486°K)

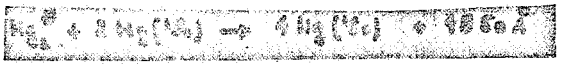
σ_a(2 body collision) $2P_0 \quad 3P_1 = 6.7 \cdot 10^{-18}$ cm^2

$3P_1 \quad 3P_0 = 3.2 \cdot 10^{-17}$ cm^2

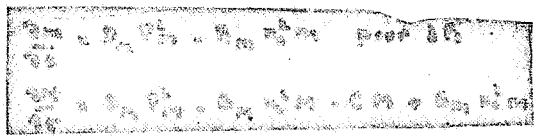
$3P_0 \quad 1S_0 = 2.2 \cdot 10^{-18}$ cm^2

$3P_1 \quad 1S_0 = 2 \cdot 10^{-22}$ cm^2

Courbey (1951-1954) studied pure mercury vapor. Formation of metastable $3P_0$ takes place through the reaction $3P_1 + 1So \rightarrow 3P_0 + 1So$. He assumes that destruction of the $3P_0$ takes place mainly by 3 body collision   with formation of an excited Hg_1* molecule which is destroyed spontaneously:  or by collision:

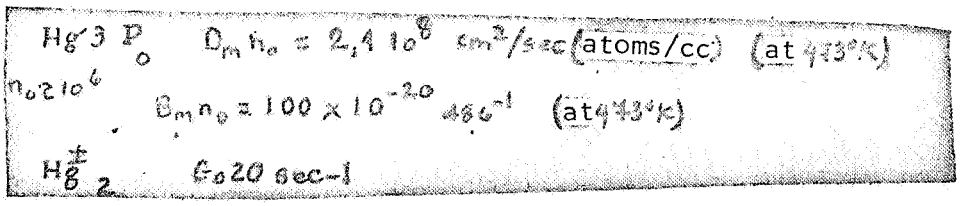


The densities of state $3P_0$ and H_{g_2}* are given by the equations



the CM term corresponding to the spontaneous destruction of the Hg_2* molecule.

From the measurement of the decrease of emission of spectrum lines 4,850 and 3,350, Courbey obtains the values of the coefficients D_m, B_m, D_m, B_m.



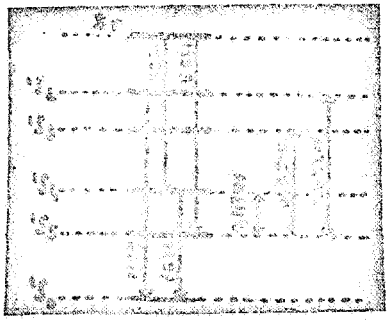
$D_M = 88\ cm^2/sec$ (200°C 10^{16} atoms/cc)

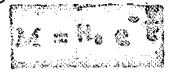
$B_M = 21\ \ 10^{-32}$ atoms/cc)$^{-2}$ sec^{-1}

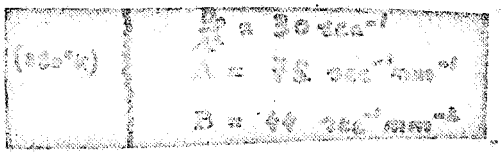
Biondi (1953) investigating the electron density in a pulse discharge within a mixture of mercury and helium, is lead to consider the reaction $Hg^m + Hg^m \rightarrow Hg^+ + e + Hg$. Proceeding exactly as in the case of pure helium (see above), he obtains equations of the following form: /44

He also obtained values (for a 2 body collision): $D_M \cdot n_e = 1.5 \cdot 10^{18} cm^2/sec$ (atom/cc) (at 350°K); $\sigma_a = 8 \cdot 10^{-17}\ cm^2$.

Krypton, metastable species 1^S5. /45



Like neon, krypton has excited states close to those of metastable species 1^S5, but these levels are sufficiently separated so that collisions with the heated particles (electrons or atoms) only participate in a negligible number of reactions going from one level to another. Smith (1963) assumes the equation  given  , then represents the density of state 1^S5 in a pulse discharge. Measurement of the value M(t) by absorption of the spectrum line of light permits determining the values of Do, A and B.



(2 body collision)

(3 body collision)

Comparison of these values with those of neon and argon shows that the destruction of the metastable particle 1^S5 through a 3 body collision is greater for krypton than for neon and argon.

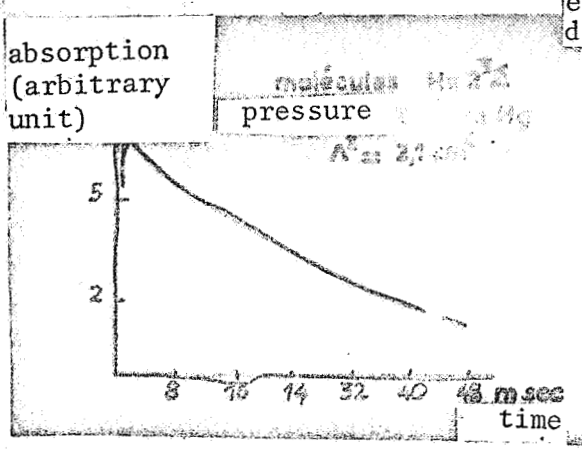


Figure III-1 (PHELPS)

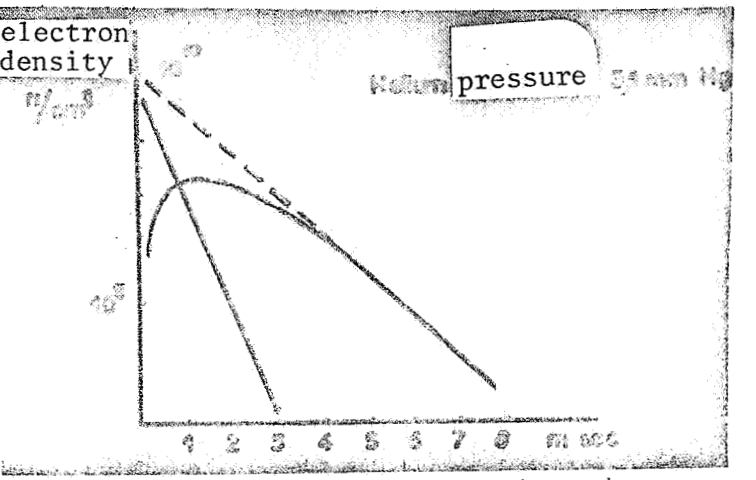


Figure III-2 (BIOBDI)

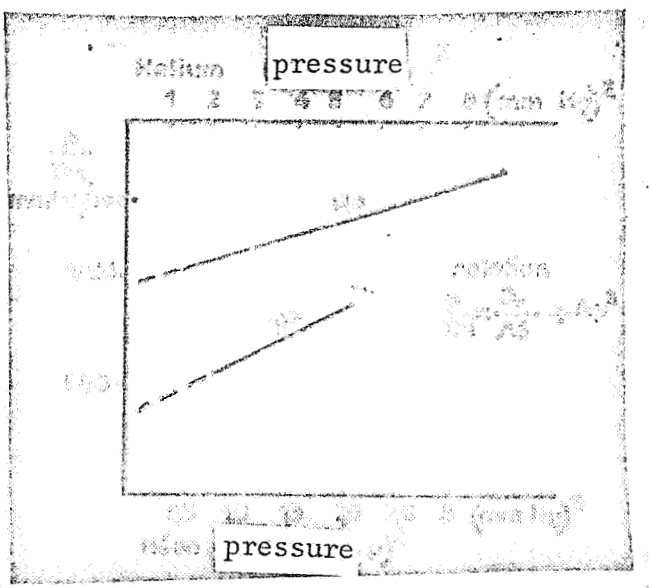


Figure III-3 (BIONDI)

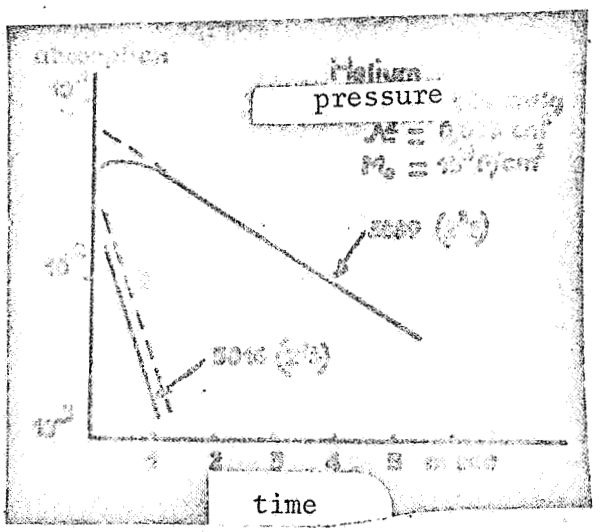


Figure III-4 (PHELPS)

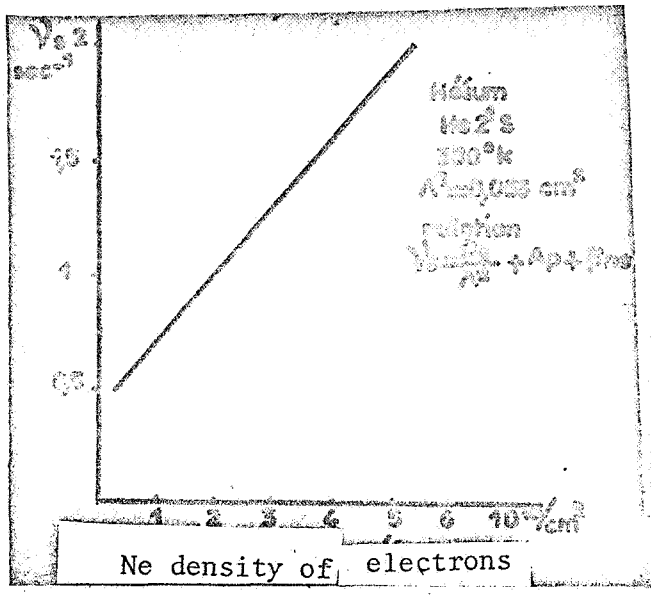


Figure III-5 (PHELPS)

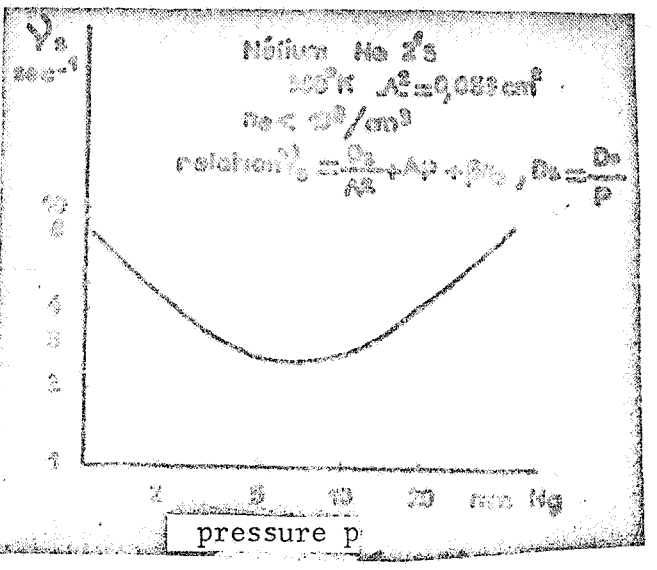


Figure III-6 (PHELPS)

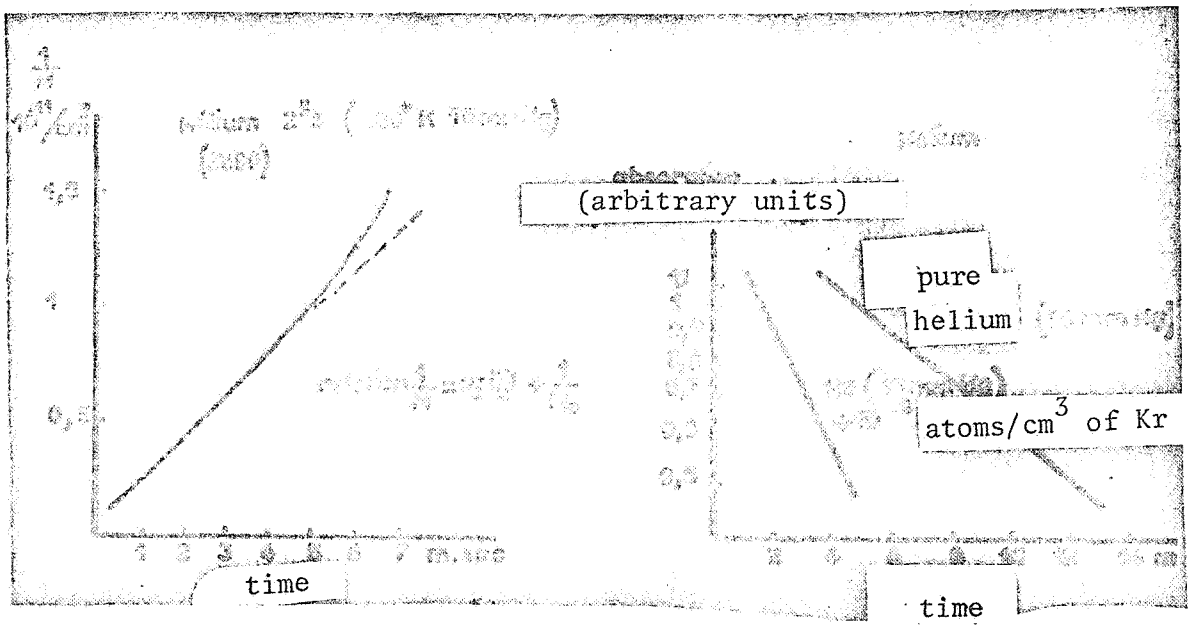


Figure III-7 (PHELPS)

Figure III-8 (BENTON)

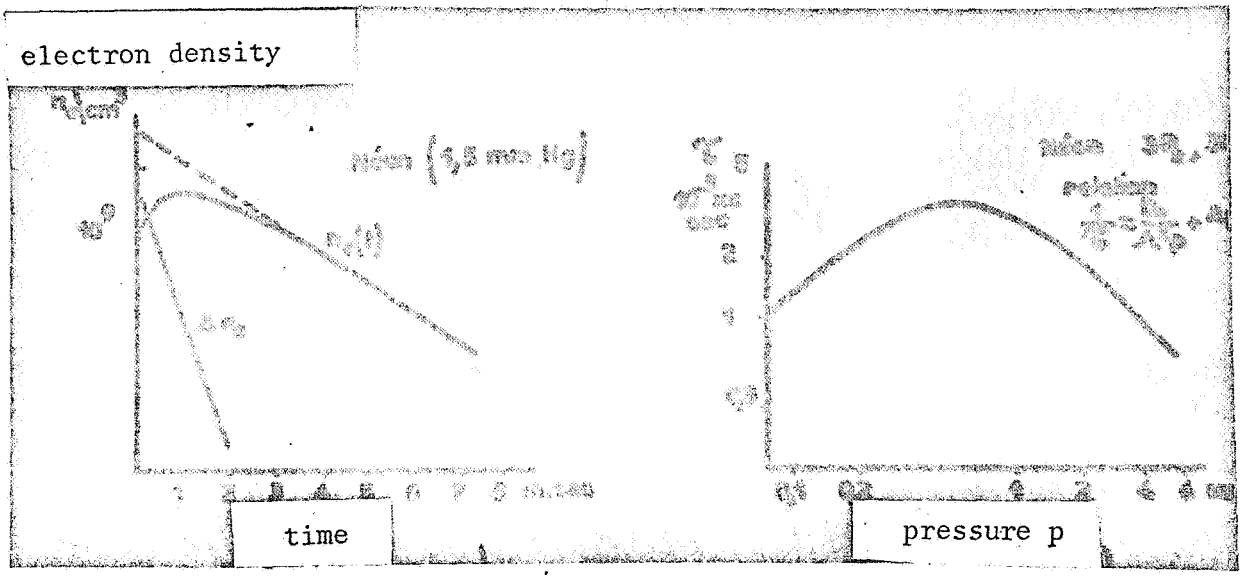


Figure III-9 (BIONDI)

Figure III-10 (DIXON)

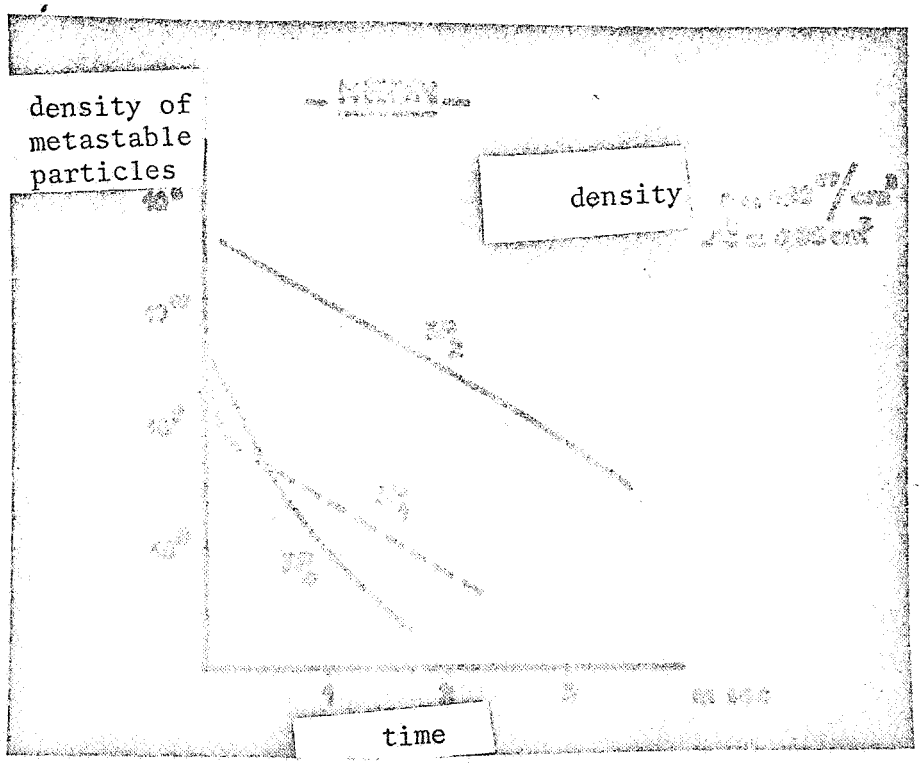


Figure III-11 (PHELPS)

CONCLUSION

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The metastable atoms investigated up to the present time may be placed in two categories:

1) those with a kinetic energy less than an electron volt (thermal energy),
2) those of high kinetic energy.

Thermal Energy Metastable Particles

The production methods (gas or beams) as well as the detection methods are known but the procedures are different. Some properties have been studied (collisions with neutral particles, electrons, and photons) but the magnitudes measured are either:

1) the results of a single experiment. For example, the measurements of effective cross sections for the reactions

$$He^m + He^m \rightarrow He^+ + He$$
$$He\,^1S + e \rightarrow He\,^3S + e$$
$$He^m + e \rightarrow He^+ + 2e$$

2) not in agreement, the differences often exceeding the experimental errors given by the experimenters. For example, the measurements of effective cross sections for the "Penning ionization" reactions.

Collisions of metastable atoms with ions have not been studied.

Metastables With High Kinetic Energy

Only the production of a beam of hydrogen metastable particles (H2S) have been studied, probably with the aim of obtaining a beam of polarized protons.

Production of These Metastable Species May Occur /4

1) By electron bombardment of a beam of fast neutral particles, but the density of such a medium is low and the effective cross section is unknown.

2) By a "charge exchange" reaction.

This method used for hydrogen may be generalized. For example, for helium and argon, the reactions

have large effective cross sections (10^{-14} cm^2) in the range form 20 to 1000 eV.

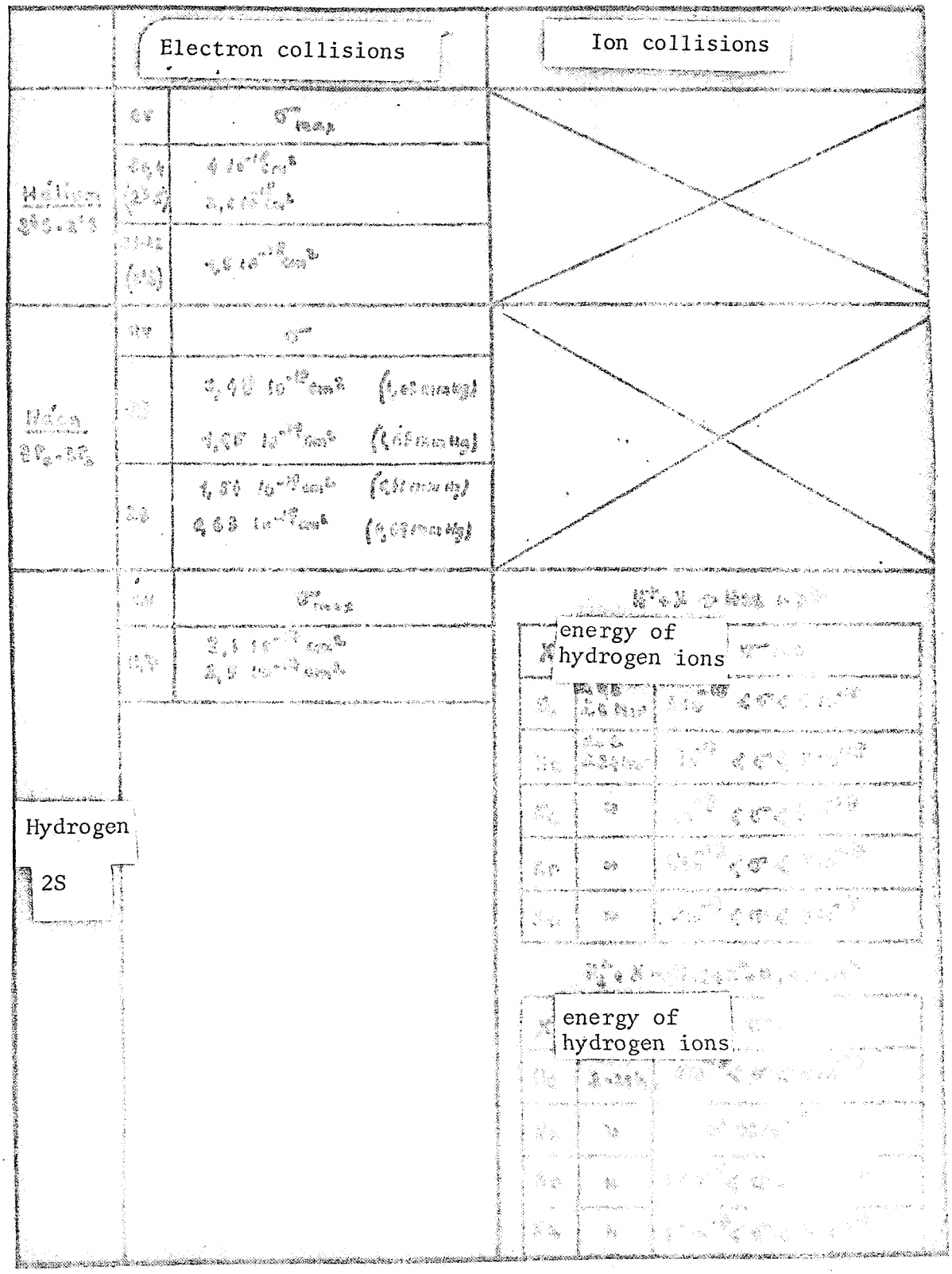
It is necessary to know which is the excited state of the neutron formed. Theoretically, the formation of a metastable or excited state is the most probable one.

It is necessary to know the destruction reactions of the metastable particles formed by collisions with atoms of Cs or Rb.

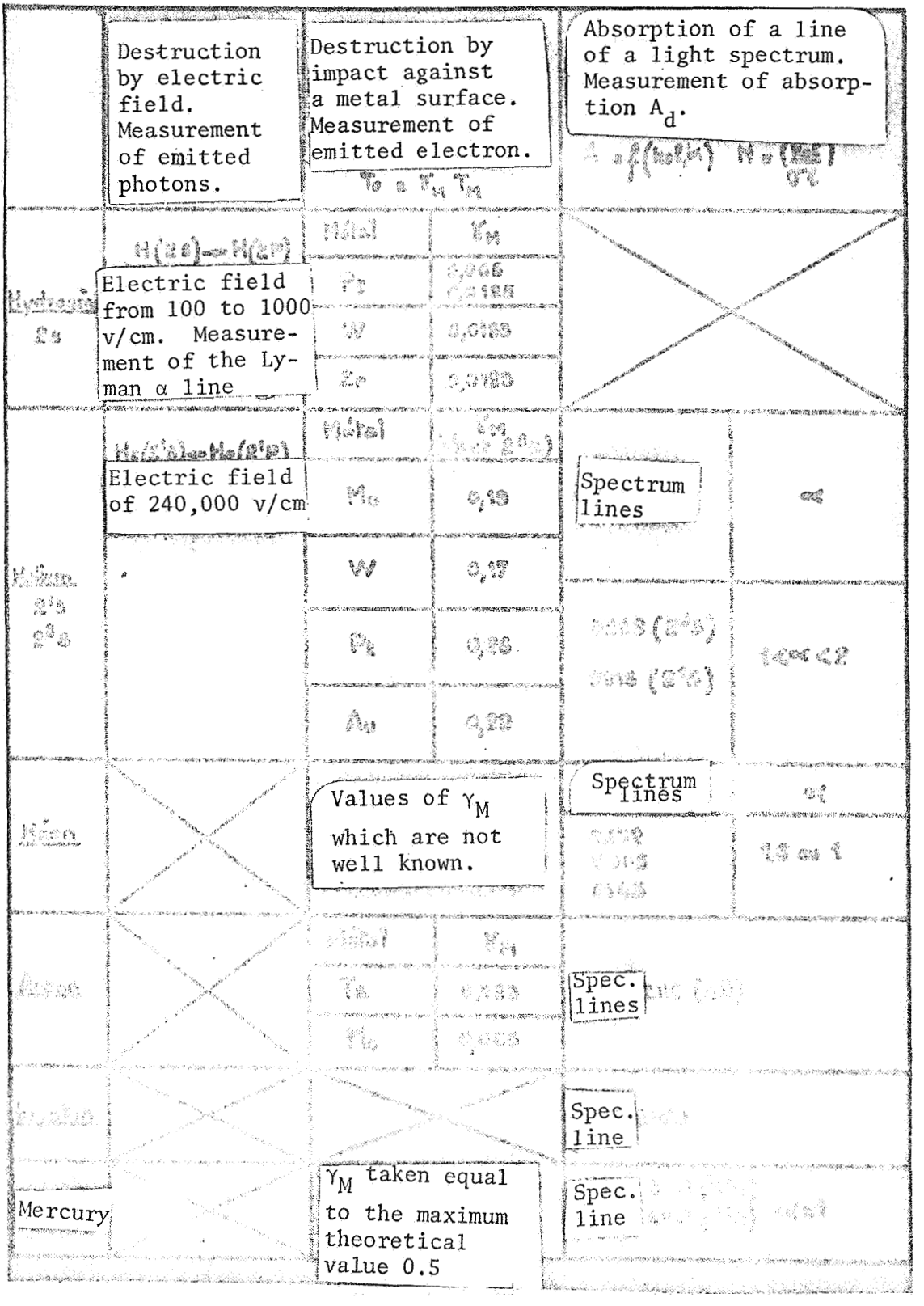
The Detection of These Metastable Particles is a Touchy Matter

The action of an electric field is practically never valid except for the hydrogen metastable species H2S and the absorption of light is not useable, since the densities are too low. The method using secondary electron emission by impact of metastable particles on a metal surface is valid in principle, but it is necessary to know the values of the emission coefficient of the metastable particles and the fast neutral particles which are generally present together.

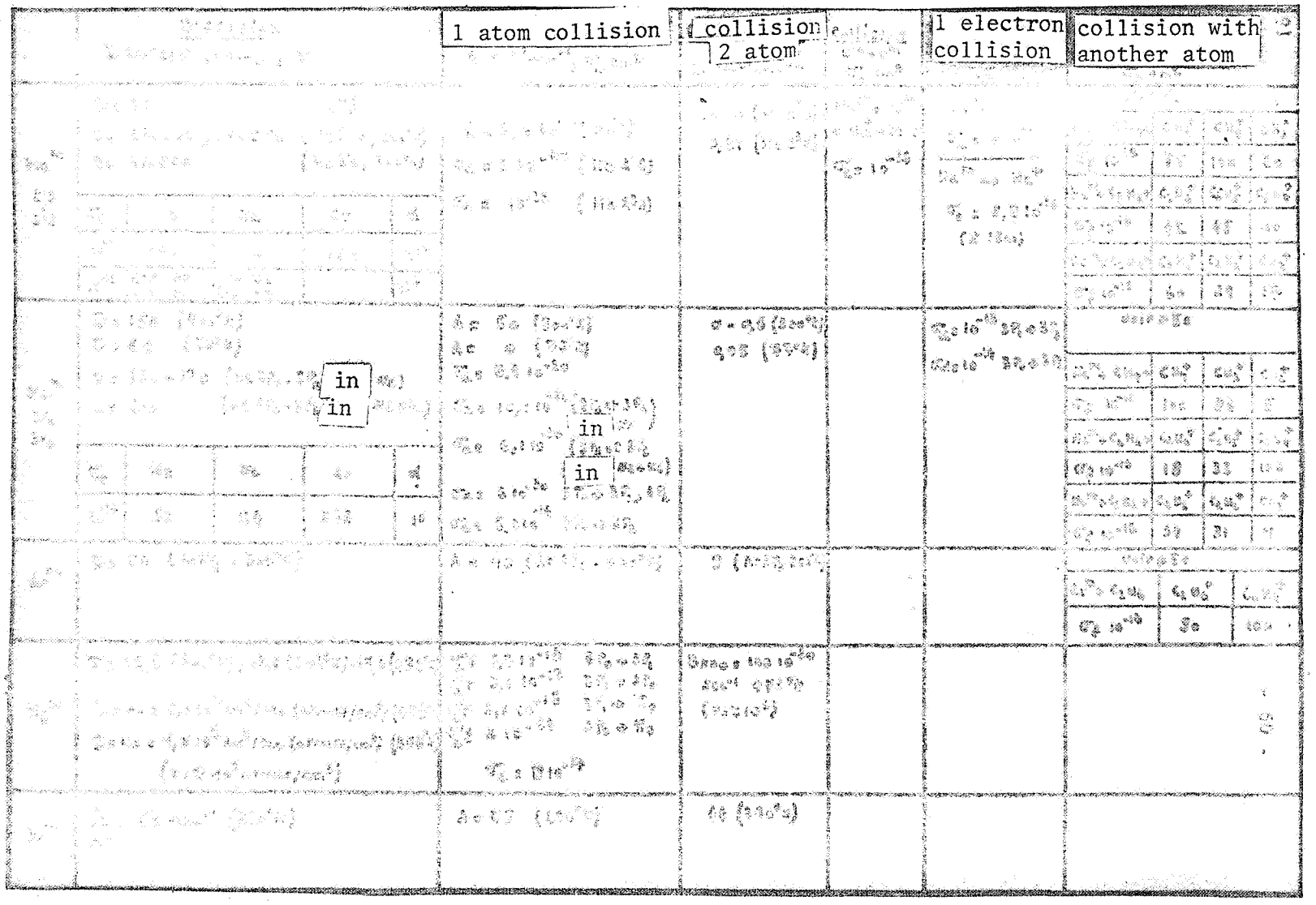
V-1 Effective Cross Sections for Production of Metastable Particles

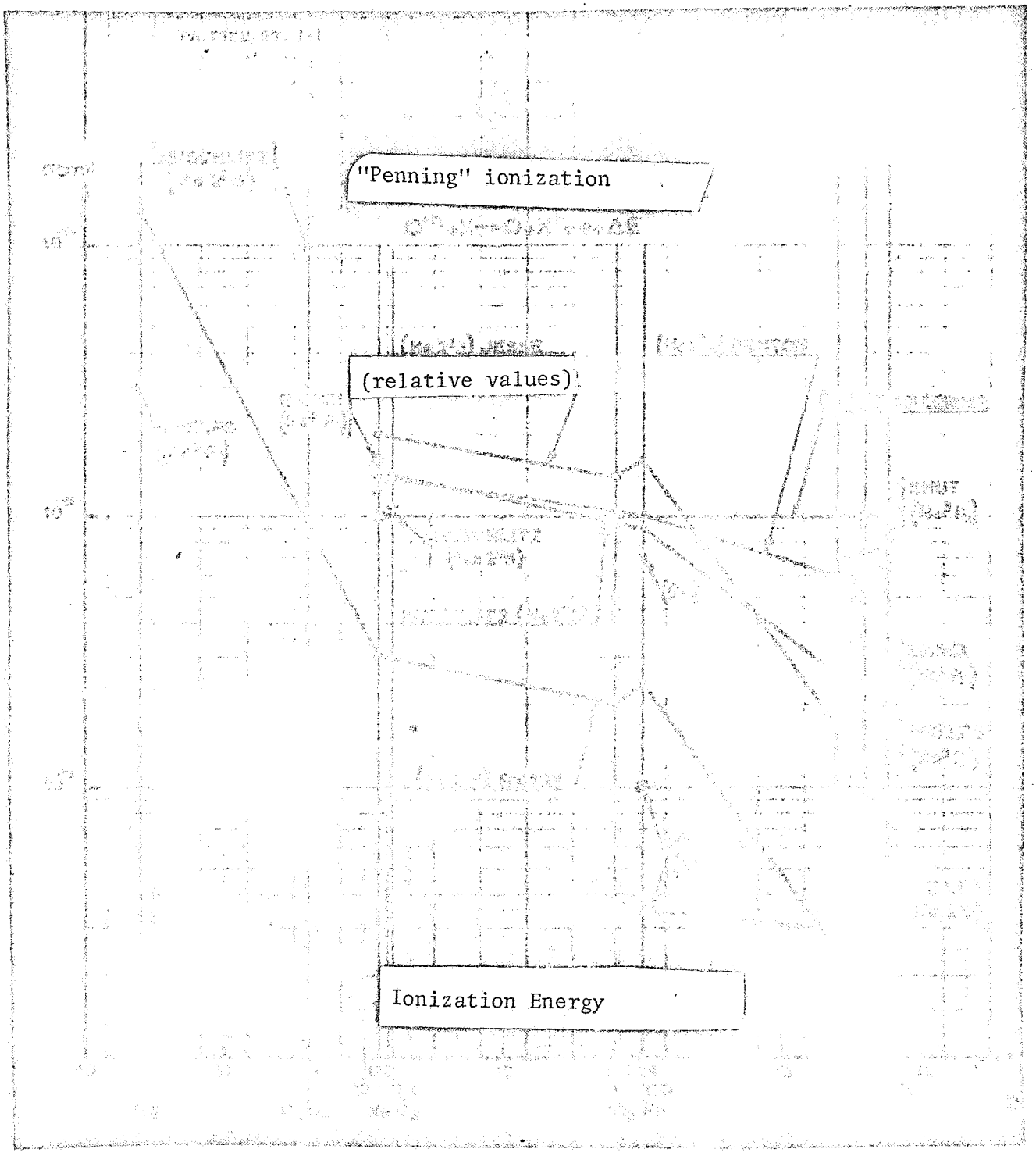


Detection of Metastable Particles



V-2 Effective Cross Sections of Destruction of Metastable Particles




"Penning" ionization
(relative values)
Ionization Energy

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